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THE FATE, PERSISTENCE AND BIOLOGICAL IMPACTS OF
DELTAMETHRIN APPLIED DIRECTLY TO AN AGRICULTURAL
POND SYSTEM AND THE PROTECTION FROM DEPOSIT
AFFORDED BY A 100 METRE SET-BACK

Surveillance Report EPS-5-AR-89-1
Atlantic Region

Canada

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The Fate, Persistence and Biological Impacts of Deltamethrin
Applied Directly to an Agricultural Pond System
and the Protection from Deposit Afforded by a 100 Metre Set-back

by

W.R. Ernst¹, R.J. Maquire², J.H. Carey², G.R. Julien¹,
J.H. Hart², R.J. Tkacz² and H.B. Lee²

¹ EPS-AR: Environmental Protection
Conservation and Protection
Environment Canada, Atlantic Region
Dartmouth, Nova Scotia

² NWRI: Inland Waters Directorate
National Water Research Institute
Burlington, Ontario

EPS-5-AR-89-1

ACKNOWLEDGEMENTS

We thank T.A. Clair, H.S. Bailey, T. Pollock, B.H. Moore and K. Kieley for help with sampling and E. Kokotich and P. Hennigar for some analyses. We thank B.D. Hill and D.C.G. Muir for advice. M.C. Gadsby and E.J. Makowski of Hoechst Canada Inc. are thanked for donations of Decis for treatments and for analytical standards. Mr. P. Hobbs of Maritime Aerial Spraying Ltd. is thanked for his co-operation and expert spraying assistance. The critical review of this manuscript by M.C. Gadsby and D.C. Muir is greatly appreciated. This work was supported in part by the Pestfund of Environment Canada.

ABSTRACT

Deltamethrin sprayed directly on a pond and its feeder stream in Prince Edward Island disappeared quickly from water, with a half-life of about 1 h. Major routes of degradation or dissipation were: (i) chemical and photochemical conversion to inactive (2 + 2')-deltamethrin stereoisomers; and (ii) hydrolysis with subsequent oxidation of products. No residues of deltamethrin stereoisomers or any of the four major degradation products sought were found 11 days post-spray. Laboratory experiments on the volatilization of deltamethrin formulations sprayed on water, as opposed to injected subsurface, indicated that volatilization from the surface microlayer was a very rapid process which could be the major route of dissipation of deltamethrin sprayed on a pond. A comparison was made of deltamethrin deposit and biological impacts between a pond which was directly oversprayed and a similar pond which was protected by a 100 metre aerial application set-back, after three spray events at each site. The effect of the set-back was to reduce measured deposit on flat plate collectors and to reduce immediate measured surface water concentrations, to 1/450 and 1/145, respectively, of that measured on with the oversprayed pond. The treatments to both ponds occurred over a range of meteorological conditions which would bracket those encountered during operational spraying. The concentrations of deltamethrin in the oversprayed pond were sufficient to cause massive mortality of caged invertebrates, high mortality to invertebrates populating artificial substrates and some mortality of caged fish. There was some caged invertebrate mortality in the set-back pond which may have been attributable to deltamethrin contamination since the concentrations measured immediately after spraying were within the range of concentrations known to be acutely lethal to some invertebrate species. No fish mortality or benthic invertebrate depletion on artificial substrates was measured in the set-back pond. The utility and effectiveness of the regulatory implementation of 100 metre set-backs during agricultural deltamethrin spraying was established.

RÉSUMÉ

Du deltaméthrin arrosé directement sur un étang et sa recharge sur l'Ile du Prince Edouard s'est rapidement dissipé dans l'eau avec une demi-vie d'environ une heure. Les principaux procédés de dégradation ou de dissipation furent: (i) conversion chimique et photochimique aux stéréoisomères inactifs (2+2')-deltaméthrin; et (ii) hydrolyse suivit de l'oxydation des produits. Aucun résidu de stéréoisomères de deltaméthrin ou des quatre produits principaux de dégradation recherchés ne furent trouvés 11 jours après l'arrosage. Des tests de laboratoire sur la volatilité des formulations de deltaméthrin arrosées sur l'eau, par opposition à l'injection sous la surface, ont démontré que la volatilisation à partir de la microcouche de surface était un procédé très rapide qui pourrait être la raison principale pour la dissipation du deltaméthrin arrosé sur un étang. Une comparaison a été faite des dépôts de deltaméthrin et des impacts biologiques entre un étang qui a été directement arrosé et un étang similaire protégé par une bande de 100 mètres suite à 3 arrosages à chaque site. L'effet de la zone de 100 mètres a été de réduire les dépôts mesurés sur des collecteurs par un facteur de 450 et de réduire les concentrations dans l'eau par un facteur de 145 lorsque comparé avec l'étang arrosé directement. Les concentrations de deltaméthrin dans l'étang arrosé directement étaient suffisantes pour causer un très haut taux de mortalité chez des invertébrés en cage, un taux de mortalité élevé aux invertébrés habitant un substrat artificiel et quelques mortalités chez des poissons en cage. Un peu de mortalité a été observé chez les invertébrés en cage dans l'étang protégé par une zone de 100 mètres sans arrosage laquelle peut être attribuée au deltaméthrin puisque immédiatement suite à l'arrosage, les concentrations mesurées atteignaient des niveaux connus comme étant toxiques à certaines espèces d'invertébrés. Aucune mortalité chez les poissons en cage ou chez les invertébrés habitant les substrats artificiels n'a été observé dans l'étang protégé. L'utilité et l'efficacité du règlement concernant l'implémentation d'une zone de 100 mètres sans arrosage durant l'application de deltaméthrin ont été établies.

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1.0 INTRODUCTION

Deltamethrin [(S)-alpha-cyano-3-phenoxybenzyl (1R,3R)-cis-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropanecarboxylate] is one of the most potent insecticides that is presently used. Its insecticidal properties were first reported in 1974 (Elliott et al. 1974) and it was developed commercially in France by Roussel Uclaf (Lhoste 1982). The cis-1R,3R configuration about the cyclopropane ring and the S configuration for the cyano group at the benzylic carbon atom are essential to its high toxicity. In Canada deltamethrin is marketed by Hoechst Canada Inc. under the trade name Decis®. Decis® is registered for use on crops including pears, tobacco, canola, mustard, potatoes, sunflowers, broccoli, cabbage, wheat and barley.

Very few reports are available on the aquatic environmental dynamics of deltamethrin. Tooby et al. (1981) found that the half-life of deltamethrin in pond water was less than 1 day. The most comprehensive work is that of Muir et al. (1985) who studied the distribution and fate of radiolabelled deltamethrin injected just below the surfaces of two small ponds. Among other things, they demonstrated that: (i) deltamethrin rapidly partitioned from water into suspended solids, plants and sediment, with a half-life of 2-4 h in water; (ii) half-lives for disappearance from sediment were 5-14 d; (iii) some of the injected deltamethrin did volatilize from water; and (iv) major products were IR cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylic acid (DBCA) and 3-phenoxybenzoic acid (PBacid). However, the analytical methods used did not differentiate between the parent deltamethrin and its less toxic isomers which can be produced by photochemical reaction or alpha proton exchange in a (dark) chemical reaction (Ruzo et al., 1977; Hill 1983; Hill and Inaba 1987; Hill and Johnson 1987). Moreover, the significance of volatilization may have been obscured by their method of introduction of deltamethrin to the ponds. The addition of deltamethrin just below the water surface (0-2 cm) likely reduced volatilization losses compared to the typical agricultural situation in which spray drift would settle on the surface microlayer of natural waters.

Although deltamethrin, like other pyrethroid pesticides, is only moderately toxic to homeotherms (Glomot 1982), it is extremely toxic to poikilotherms such as aquatic invertebrates and fish (Khan 1983). Zitko et al. (1979) determined that the 96-hour lethal threshold of deltamethrin for lobster (Homarus americanus) is 1.4 ng/L. Field data for deltamethrin residue concentrations in water after operational use are not readily available. Theoretical calculations would indicate, however, that at the normal application rate of 5 to 7.5 g ai/ha used on vegetable crops in Canada, a direct overspray of watercourses 10 cm in depth could result in deltamethrin concentrations of 5 to 7.5 ug/L. These concentrations would obviously greatly exceed the concentrations necessary to cause mortality in aquatic fauna. For this reason, buffer zones of 15 m and 100 m have been established to protect water bodies when deltamethrin is sprayed from the ground or air respectively.

Despite these precautions some deltamethrin may drift to water and it is necessary to characterize the aquatic persistence and fate of this highly toxic insecticide. In addition, there has been no empirical evidence published to this date which indicates whether the buffer zones are effective in preventing biological impacts.

We report here the persistence, fate and effects of deltamethrin sprayed aerially on two ponds in Prince Edward Island, Canada. This work extends that of Muir et al. (1985) by: (i) assessing the importance of volatilization from the surface microlayer in laboratory experiments, and (ii) determining the concentrations of the four sets of enantiomers which result from sunlight photolysis of deltamethrin, as well as concentrations of DBCA, PBacid, 3-phenoxybenzaldehyde (PBald) and 3-phenoxybenzyl alcohol (PBalc) which are major, but certainly not the only, products of the photolysis of deltamethrin (Ruzo et al. 1977), its degradation on and in plants (Ruzo and Casida 1979; Khan et al. 1984; Akhtar and Khan 1985) and its metabolism by mammalian and other enzyme systems (Ruzo et al. 1978, 1979; Shono et al. 1979; Akhtar 1984; Akhtar et al. 1985, 1986).

The magnitude of the biological impact associated with direct deposit in a pond system was also assessed by observing mortality in caged fish and invertebrates and quantifying colonization of artificial substrates by invertebrate species. In addition, the protection to pond ecosystems afforded by watercourse buffer zones was assessed by comparing deposit and biotic disruption in the oversprayed pond with that of a pond protected by a 100 metre buffer zone.

2.0 METHODS AND MATERIALS

There are 8 possible stereoisomers of deltamethrin. We have used the numbering system given by Ruzo et al. (1977) in which the parent deltamethrin is designated as 1 and the only other isomer which is toxic to insects (Tessier 1982) or mice (Ruzo et al. 1977), although to a lesser extent in each case, is designated as 3. On achiral gas chromatographic phases there are thus four pairs of enantiomers which can be separated, (1+1'), (2+2'), (3+3') and (4+4'). Of these, only the (1+1') and (3+3') pairs appear to be of insecticidal and mammalian toxicological importance. It is recognized that each of these pairs is potentially the sum of an active and an inactive enantiomer. There is no information on the toxicity of deltamethrin isomers to aquatic organisms. Although commercially available deltamethrin is greater than or equal to 97% active isomer 1, for the purposes of this paper we have designated the parent insecticide as (1+1')-deltamethrin since achiral chromatographic phases were not used in the analyses.

2.1 Laboratory Tests of Deltamethrin Stability and Volatilization

Tests were done in the laboratory to determine the stability of (1+1')-deltamethrin in sterilized pond water, and to determine the relative importance of volatilization from water. In one set of experiments, a Decis formulation was injected 2 cm below the surface of 0.5% (w/v) azide-poisoned pond water in 125 mL glass jars. The initial deltamethrin concentration was 2 ug/L. Duplicate samples were extracted at intervals over 1 month and the deltamethrin isomers, but not degradation products, were determined. The whole volume of the water sample was extracted, and care was taken to rinse the inside of the jars thoroughly to minimize adsorptive loss of deltamethrin. In the other set of experiments a Decis formulation was sprayed (using a sprayer of the type used to develop thin layer chromatograms) at an estimated rate of 6 g ai/ha (average field rate) over jars of 0.5% (w/v) azide-poisoned pond water in an effort to determine if volatilization from the surface microlayer was significant. Replicate samples were extracted at intervals over 1 month and the deltamethrin

isomers, but not degradation products, were determined. Both sets of experiments were carried out at 20°C in darkened fume hoods to eliminate photolytic degradation.

2.2 Analytical Materials

Analytical standards of deltamethrin and DBCA were provided by Hoechst Canada Inc. Decis 2.5 EC emulsifiable deltamethrin concentrate in xylenes from Hoechst (lot No. DEREHE0101) was bought locally and found, by GC-ECD, to contain only one peak corresponding to (1+1')-deltamethrin at the nominal concentration of 25 g/L, even 1.5 y after purchase. As noted above, it is assumed that only the parent enantiomer 1 was present, but since the analytical method can not indicate otherwise, the designation (1+1')-deltamethrin will be used in this paper.

3-Phenoxybenzaldehyde (PBald), 3-phenoxybenzyl alcohol (PBalc), 3-phenoxybenzoic acid (PBacid) and pentafluorobenzyl bromide (PFBBBr) were obtained from Aldrich Chemical Co., Milwaukee, WI. Pesticide grade dichloromethane, pentane, hexane, acetone, methanol, benzene, and toluene were all obtained from Caledon Laboratories, Georgetown, ON.

The sodium sulfate, silica gel, aluminum foil, glass fibre filters and disposable pipets were heated to 500°C for 24 h before use. All glassware was rinsed with pesticide grade solvents before use, as were the 40 L extraction vessels used in the field work. Hydrochloric acid was reagent grade, but was extracted with pentane before use.

A mixture of the (1+1'), (2+2'), (3+3') and (4+4') diastereoisomers of deltamethrin was prepared from the (1+1') analytical standard by the procedure given by Hill and Johnson (1987). Deltamethrin, as a thin film (15 ug/cm²) on glass, was irradiated outdoors with bright summer sunshine for 4 d, and the photoisomers were recovered from the glass with hexane. The electron capture responses of all diastereoisomers were assumed to be identical to that of the (1+1') analytical standard.

2.3 Spray Site Locations

The oversprayed study site, was located at Kelvin Grove, in a potato-growing area of Prince Edward Island 5 km south of Kensington (Fig. 1 and 2). The pond was about 0.4 ha in area and was bordered on the northeast by a 10 ha grain field and on the southwest by a 20 ha potato field. The area to the southeast and the northwest was primarily bullrushes (*Typha* sp.) and alders (*Alnus* sp.) which were approximately 4 m in height. The pond was shallow, 2 m deep at its deepest point. The pond was fed by a stream (approximately 0.25 m³/s) but it was not a direct flow-through system. The temperature of the pond and stream water at the time of spraying was 9°C and the pH was 7.7.

The pond which was to be protected by the 100 m set-back was located at Cape Traverse, 22 km south of Kensington. This pond (Fig. 3) was approximately 0.2 ha in size and was bordered on the northwest by a grain field approximately 20 ha in size and to the southeast by a potato field approximately 30 ha in size. The pond was almost entirely surrounded by alders 4 m in height, with the exception of the western edge where the alders had been cut to a height of 0.5 m to allow a direct path for any spray cloud moving from the grain field. This pond was also shallow, being no more than 1 m in depth and was more of a flow-through system than the oversprayed pond. This pond was fed by a stream with an estimated flow rate of approximately 0.025 m³/sec.

2.4 Spray Application

Sprays were applied at each site using conventional agricultural application equipment, formulation and dosage rates. The application parameters are contained in Table 1. Meteorological conditions at the time of spraying can affect the amount of pesticide which is deposited at the target site (Armstrong 1977) and which drifts off-target (Warren 1976). At the overspray site, a U2A meteorological station with a 10 m mast was erected. This provided continuous measurement of windspeed, wind direction

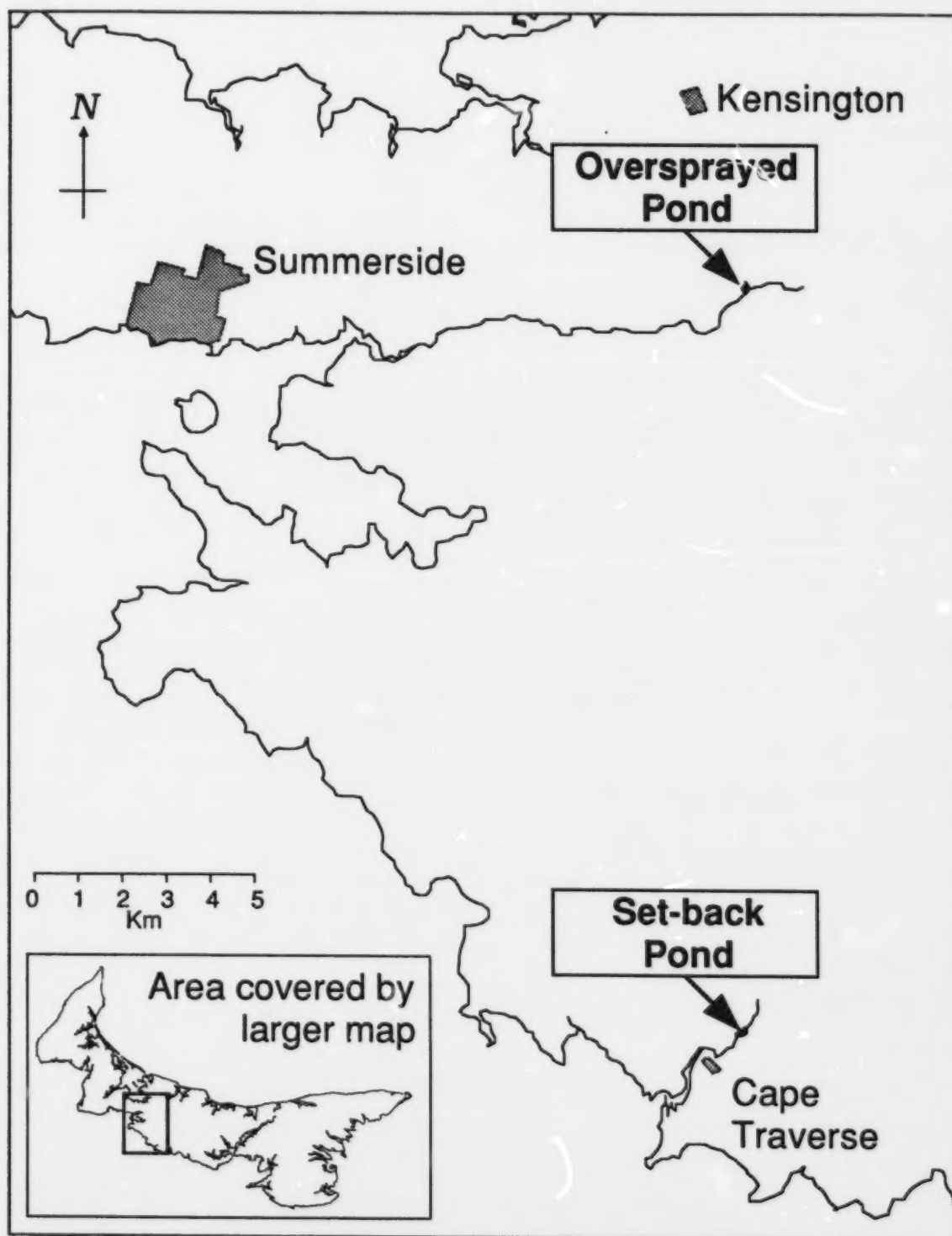


FIGURE 1 LOCATION OF STUDY SITES IN PRINCE EDWARD ISLAND

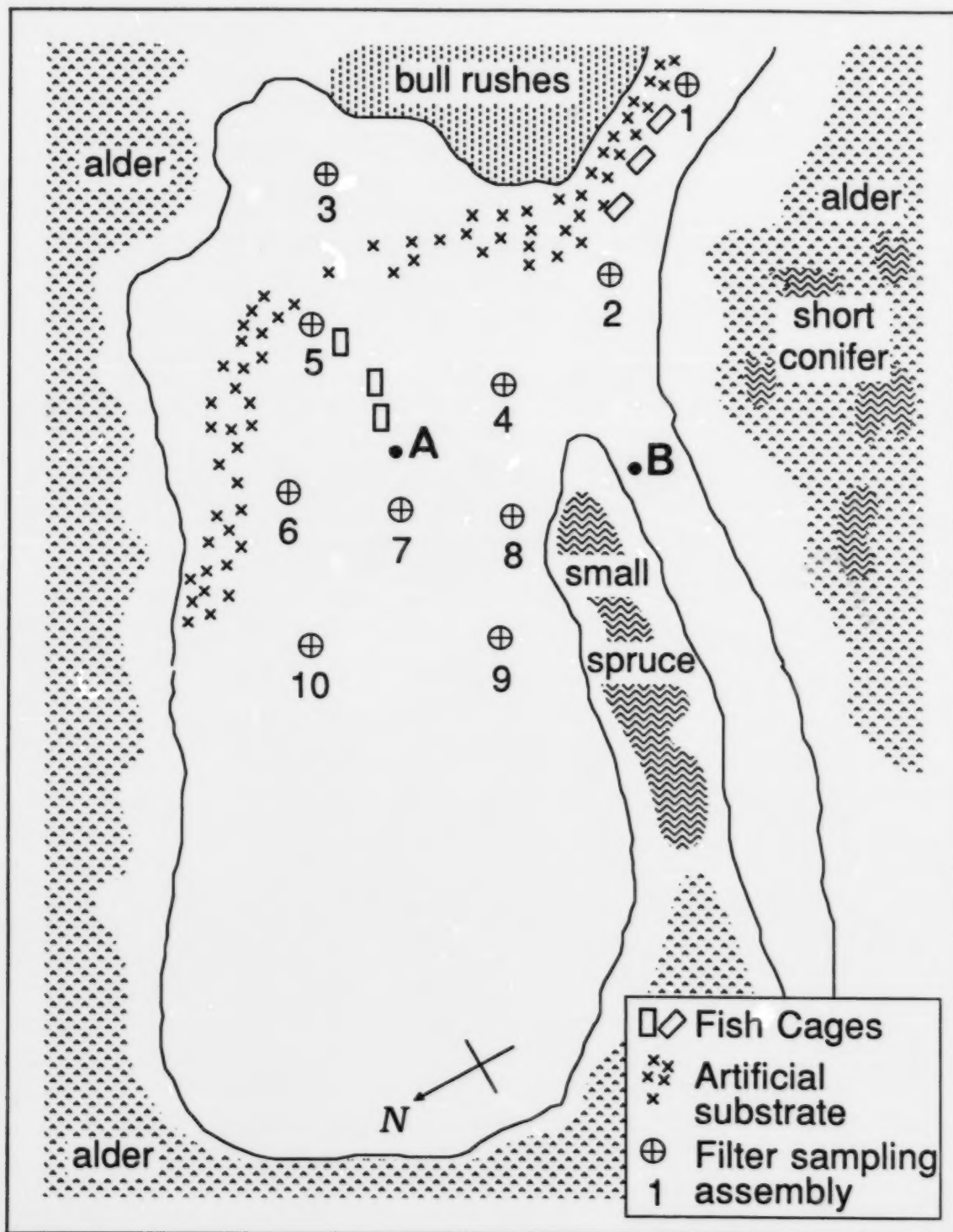


FIGURE 2 DIAGRAM OF OVERSPRAYED SITE

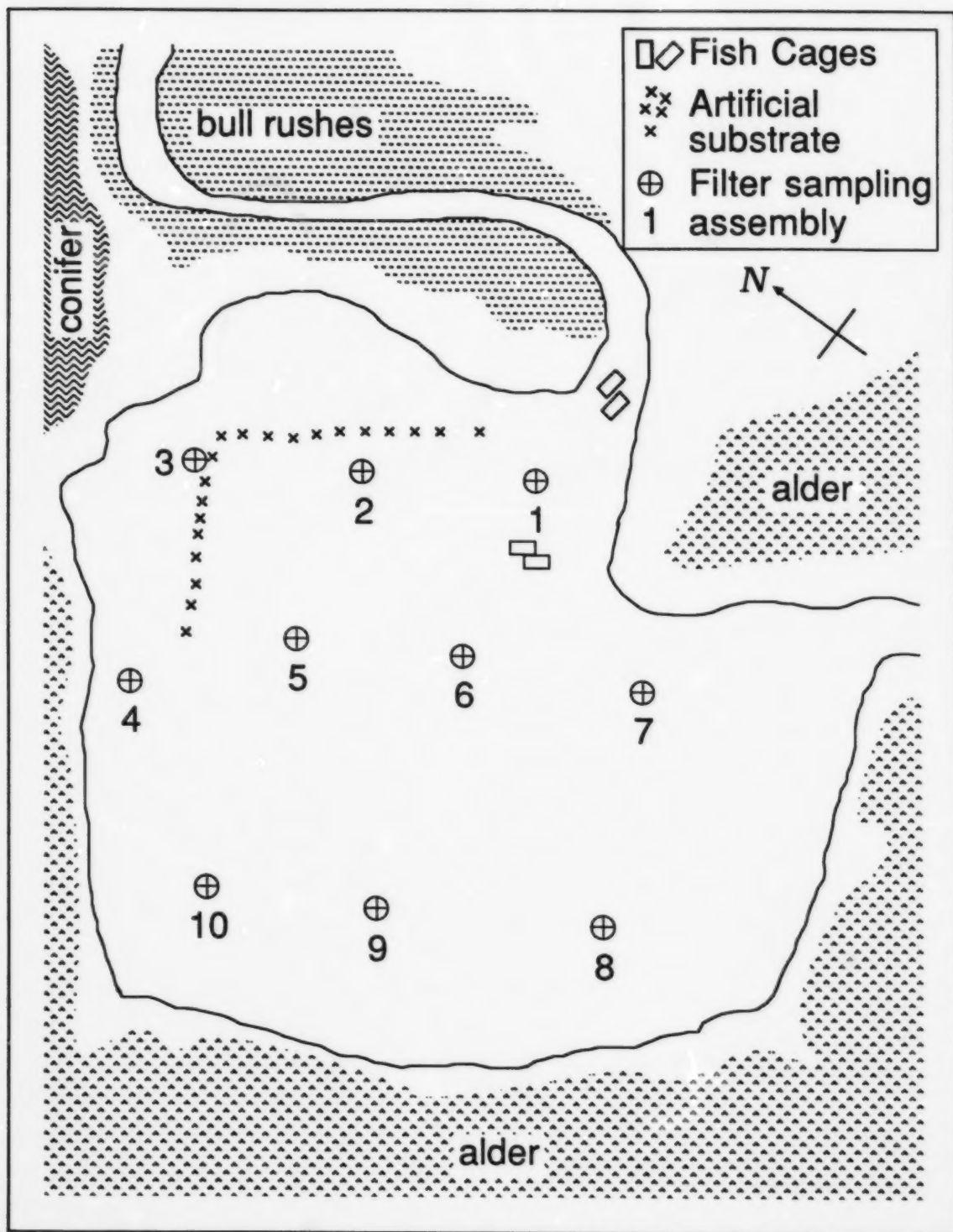


FIGURE 3 DIAGRAM OF SET-BACK SITE

TABLE 1 - APPLICATION PARAMETERS

Rate:	28.06 L/ha
Mixing Rate:	6 L DECIS 2.5 EC/681 L water
Dosage Rate:	6.18 g ai/ha
Nozzles:	24 TEE-JET D6-45
Airspeed:	163 km/h
Boom Pressure:	310 K Pa
Swath Width:	34 m
Boom Height:	2.5 m
Droplet Size:	350 um VMD*
Aircraft:	Grumman AG-CAT

*Manufacturer's specifications

and air temperature at 10 m. Pertinent meteorological conditions are contained in Table 2. Those presented for Kelvin Grove were obtained from the on-site meteorological station while those presented for the set-back site were obtained from CFB Summerside, which is approximately 30 km from the spray site. Due to the location of the alder cut at the set-back pond, all spray events were planned to occur under approximately the same wind direction. At the set-back pond spraying occurred under varied wind speed conditions ranging from 3.6 to 11.2 km/h. Spraying under the highest windspeed condition (actually somewhat higher than the 8 km/h recommended on the product label) represents one of the worst cases for pesticide drift to the pond. At the Kelvin Grove site, the pond was directly oversprayed when the adjacent fields were treated, and at the same dosage rate. The entire pond was sprayed, as well as the stream, from a point 50 m downstream to 100 m upstream of the sampling points. At the overspray site, intensive chemical sampling was conducted to determine the deltamethrin degradation patterns.

At the Cape Traverse site, permanent markers were placed in the adjacent fields at 100 m from the pond edge to indicate the edge of the spray area and buffer zone for the pilot.

2.5 Sampling

2.5.1 Fate of Deltamethrin

Sampling was done intensively at intervals which decreased logarithmically from 0.2 to 55 hours post spray at one location (A) in the pond and one location (B) in the stream (Fig. 2). The pond site was chosen in order to elucidate the degradation pattern of deltamethrin without the complication of water flow.

Samples were also taken, although less frequently, at two other points in the stream at the oversprayed site. Site D was approximately

TABLE 2 - METEOROLOGICAL CONDITIONS AT TIME OF APPLICATION

Site	Date	Time	Air Temp. (°C)	R.H. (%)	Wind Speed (m/s)(km/h)		Wind Direction (°)
Over Sprayed Pond (Kelvin Grove)	July 10, 1986	0730	12.2	79	3.0	10.8	282
	July 22, 1986	0600	7.1	100	0.1	0.4	007
	August 8, 1986	0810	19.3	96	1.5	5.4	187
Setback Pond (Cape Traverse)	July 16, 1986	0645	13.0	94	3.1	11.2	280
	August 13, 1986	0630	13.0	87	1.0	3.6	240
	August 26, 1986	1930	16.0	68	1.5	5.4	240

2 km downstream of the spray site. Site C was approximately 0.5 km upstream of the spray site. Analyses of samples collected from the upstream Site C before and up to 11 d after the spray showed only the infrequent occurrence of very low concentrations of DBCA and (1+1')-deltamethrin (< 2 ng/L), which may have been due to contamination during sample handling or unrelated spraying of deltamethrin upstream.

2.5.1.1 Subsurface water (Sites A and B)

Forty-litre samples were collected from a depth of 0.5 m and immediately pressure filtered through 0.45 μ m glass fibre filters using compressed N_2 and modified pressurized beverage containers, pressure filters and Teflon transfer lines (Fox 1986). The filters containing the suspended solids were frozen for shipment to the laboratory. The filtrate was immediately acidified to pH 1 and extracted twice with dichloromethane (1 L each time, with stirring for 10 min) in the 40-L containers. After phase separation the dichloromethane extracts were transferred to amber solvent bottles for shipment to the laboratory. Some of the extracted water was added to each bottle to retard volatilization of the dichloromethane. It is recognized that passage through a 0.45 μ m filter is only an operational definition of the "dissolved" phase and that chemicals such as deltamethrin may still be adsorbed to colloidal material which passes the filter.

2.5.1.2 Sediment (Site A only)

The top 2 cm of substrate was collected with a scoop from an area at which the water depth was 0.3 m, and the sediment was transferred to darkened 500-mL glass jars with aluminum foil-lined screw caps. The sediment jars were then frozen for transport to the laboratory.

2.5.1.3 Surface microlayer (Site A only)

A rotating drum sampler with ceramic coating was used, similar to that designed by Harvey (1966). The radius was 15 cm and the length 48 cm.

The operation of the drum was calibrated so that in the collection of 4 L of microlayer in 10 min at 12 rpm, the thickness of the microlayer sampled was estimated to be 75 μm .

The 4-L surface microlayer samples were collected as soon as possible after the spray and were not filtered, i.e., they were analyzed as bulk water. Decanted into amber solvent bottles, the samples were acidified to pH 1 for preservation, and 200 mL dichloromethane was added to start extraction. The contents were shaken several times and then transported to the laboratory where they were more thoroughly extracted with dichloromethane.

2.5.1.4 Other Samples

Two other kinds of samples were taken to provide additional information on the persistence, transport and fate of deltamethrin in aquatic environments.

Larger amounts of suspended solids (up to 3 g) were obtained from the stream at Sites B, C and D at various times before and after the spray in order to improve the detection limits for deltamethrin isomers and degradation products in suspended solids. The samples were obtained by pumping 260 L of water through a Westphalia continuous flow centrifuge. The centrifuge retains solids of roughly the size retained by a 0.45 μm filter. The suspended solids were preserved in the same way as the sediment.

2.5.2 Extraction and Analysis

The methods used for the extraction, clean-up and analysis of the water, sediment, and suspended solids were developed for deltamethrin isomers and the four degradation products DBCA, PBald, PBalc and PBacid.

2.5.2.1 Extraction

Dichloromethane extracts of the filtered subsurface water samples and the unfiltered surface microlayer samples were dried by passage through sodium sulfate and concentrated to 10 mL.

Frozen sediment and suspended solids samples were freeze dried and extracted in a Soxhlet apparatus with dichloromethane for 24 h at 8 cycles/h. Ten g of sediment and all suspended solids collected were extracted. The extracts were passed through sodium sulfate and concentrated to 10 mL.

Some sediment samples which had been extracted with dichloromethane were mixed with 6N HCl at 50°C for 24 h in an effort to release any bound or conjugated residues of (1+1')-deltamethrin and its isomers and degradation products, but no such residues were found.

2.5.2.2 Preliminary clean-up of sediment, and suspended solids

The 10-mL dichloromethane extracts from above were solvent-changed to pentane by addition of pentane and careful evaporation to 0.5 mL with a gentle flow of nitrogen. This procedure was repeated three times to remove traces of dichloromethane. The extract was then made up to 1 mL pentane. At this point there was usually some precipitation in the test tube, but all material was transferred to the clean-up column in the course of the four-fraction clean-up described below.

The 1-mL pentane extracts were cleaned up on activated silica gel columns of length 40 cm and diameter 2.5 cm, with a layer of sodium sulfate for drying. Four 100-mL fractions were eluted from the columns. Fraction 1 was pentane; fraction 2 was dichloromethane/pentane (20/80, v/v); fraction 3 was dichloromethane/pentane (60/40, v/v); fraction 4 was 50 mL dichloromethane followed by 50 mL methanol. At each solvent change, a

small amount of that particular solvent was used to rinse the test tubes ensuring that even the precipitated material was transferred to the clean-up column. All four fractions were solvent-changed to pentane and reduced to 10 mL. The deltamethrin isomers and degradation products usually eluted in fractions 1 to 3. The fractions were split and analyzed as described below.

2.5.2.3 Analytical scheme

The extracts of water and the cleaned-up extract fractions from sediment, suspended solids and potato leaves were analyzed according to the scheme shown in Figure 4. In brief the samples were split, deltamethrin isomers, PBald and PBalc were determined by gas chromatography with an electron capture detector (GC-ECD) or a mass spectrometric detector (GC-MSD), and the DBCA and PBacid were determined as their pentafluorobenzyl derivatives by GC-ECD. All sample extracts were concentrated to 1.0 mL before analysis.

Derivatization of the samples with pentafluorobenzyl bromide (PFBBBr) involved concentrating each sample to 4.0 mL acetone solution, adding 30 μ L 30% K_2CO_3 , 100 μ L 5% PFBBBr solution in acetone, and heating for 3 h at 60°C. After the reaction, acetone was replaced with hexane and the reaction mixture was cleaned up on a 5 cm 5%-deactivated silica gel column made with a disposable pipet. Ten mL hexane was passed through the column and discarded. Then 10 mL toluene or benzene was passed through the column and collected. This fraction contained the DBCA-PFB and PBacid-PFB derivatives.

Analyses for deltamethrin and its isomers was performed with a Varian 3400 gas chromatograph and an electron capture detector. A 30 m x 0.2 mm id DB-1 column with 10:1 split was programmed from 220 to 235°C at 0.5°C/min followed by a 10 min hold. The inlet temperature was 200°C. With these conditions partial separation of the four sets of enantiomers was achieved similar to that described by Hill and Johnson (1987). Because

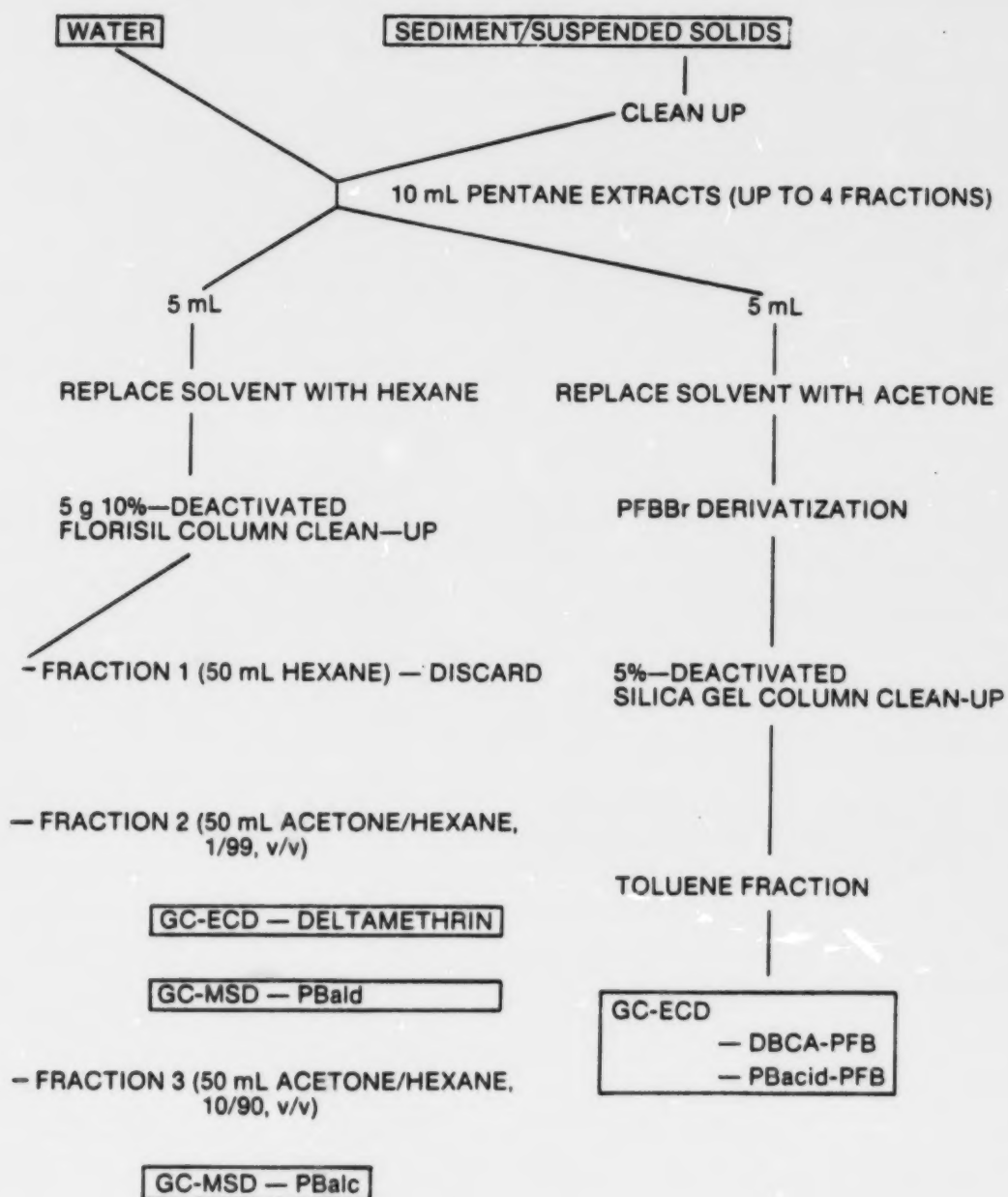


FIGURE 4 ANALYTICAL SCHEME FOR DELTAMETHRIN ISOMERS AND SOME DEGRADATION PRODUCTS IN EXTRACTS OF WATER, SEDIMENT AND SUSPENDED SOLIDS

the DB-1 column was achiral and did not separate enantiomers, each of the four chromatographic peaks potentially represents one or both of the possible enantiomers. Using the numerical designation of Ruzo et al. (1977), the retention times and peak identities were assigned in the same way as Hill and Johnson (1987): 21.9 min, (2+2'); 22.9 min, (4+4'); 23.3 min, (1+1'); and 24.0 min, (3+3').

Analyses for the DBCA-PFB and PBacid-PFB derivatives were performed with a Hewlett-Packard 5880A gas chromatograph and an electron capture detector. A 12 m x 0.2 mm id OV-1 column was used under the following conditions: initial temperature 70°C for 0.5 min; programming rate 1, 30°C/min (70-200°C); rate 2, 5°C/min (200-280°C); with final hold for 15 min. Under these conditions the retention times of the PFB esters of DBCA and PBacid were about 8.9 and 12.1 min, respectively. Some analyses for these compounds were also done with the Varian 3400 gas chromatograph with a 30 m DB-1 column under similar conditions.

For BPald and PBalc, analyses were done with a Hewlett-Packard 5880A gas chromatograph and 5970B mass selective detector and data system. A 30 m x 0.25 mm id SPB-5 column was directly interfaced to the electron-impact ion source for maximum sensitivity. Electron energy was 70 eV. Operating conditions were: injection port, 275°C; interface, 280°C; column head pressure 4 psi; and helium carrier gas. Gas chromatographic conditions were: initial temperature, 70°C for 0.5 min; programming rate 1, 25°C/min (70-180°C); and rate 2, 2°C/min (180-220°C). The ions selected for monitoring for PBald and PBalc were 198 and 200, respectively, and the retention times were 10.2 and 11.5 min, respectively. Other, less sensitive, analyses for these two compounds were performed by GC-ECD on highly concentrated (approximately 10 uL) samples under similar conditions.

In experiments in all-glass containers, recoveries of (1+1')-deltamethrin, DBCA, PBald, PBalc and PBacid from water at spiked levels of 5 ng/L were in the range 88-115%. From sediment, recoveries for these

compounds were in the range 65-109%. It is assumed that recoveries of other isomers of deltamethrin would be the same as for the (1+1')-deltamethrin. Recoveries of deltamethrin and degradation products from water using the modified pressurized beverage containers were not determined, but are assumed to be the same as recoveries from all-glass containers. Using the beverage containers, Fox (1986) demonstrated recoveries in the range 56-118% for a variety of chlorinated hydrocarbons spiked at 1 ng/L in Lake Ontario water. The concentrations reported in this article have not been corrected for recovery. The limits of quantitation (Keith et al. 1983) for the compounds of interest in water and sediment, respectively, are: (1+1')-deltamethrin, 0.1 ng/L and 0.5 ug/kg dry weight; DBCA, 0.2 ng/L and 1 ug/kg; PBald, 0.5 ng/L and 2 ug/kg; PBalc, 0.5 ng/L and 2 ug/kg; and PBacid 0.2 ng/L and 1 ug/kg.

2.5.3 Deposit Sampling

Ten deposit samplers were evenly distributed on the surface of each pond (Figure 5). These samplers consisted of a 20 cm x 25 cm stainless steel plate which had been fixed to a 2 cm wooden dowel 50 cm in length. The dowel was weighted on one end and ran through the centre of a styrofoam float. The construction of the samplers was such that the plates were approximately 30 cm above the pond's surface when deployed. Prior to each spray, the plates were rinsed with pesticide grade hexane and Gelman (20.3 x 25.4 cm) glass fiber filters, which had previously been washed with hexane, were placed on the plates and secured with paper clips. These filters were removed with forceps 15 min after the last swath of the aircraft, and placed in nitrogen-filled, 500-mL glass jars which had previously been detergent washed and rinsed with distilled water/hexane. The jars were then frozen and transported to the EP laboratory in Dartmouth where they were analyzed for deltamethrin content.

At the time that deposit filters were removed, 800-mL water samples were obtained from the same location. Water samples were obtained in 1-L amber glass bottles which had previously been detergent washed and

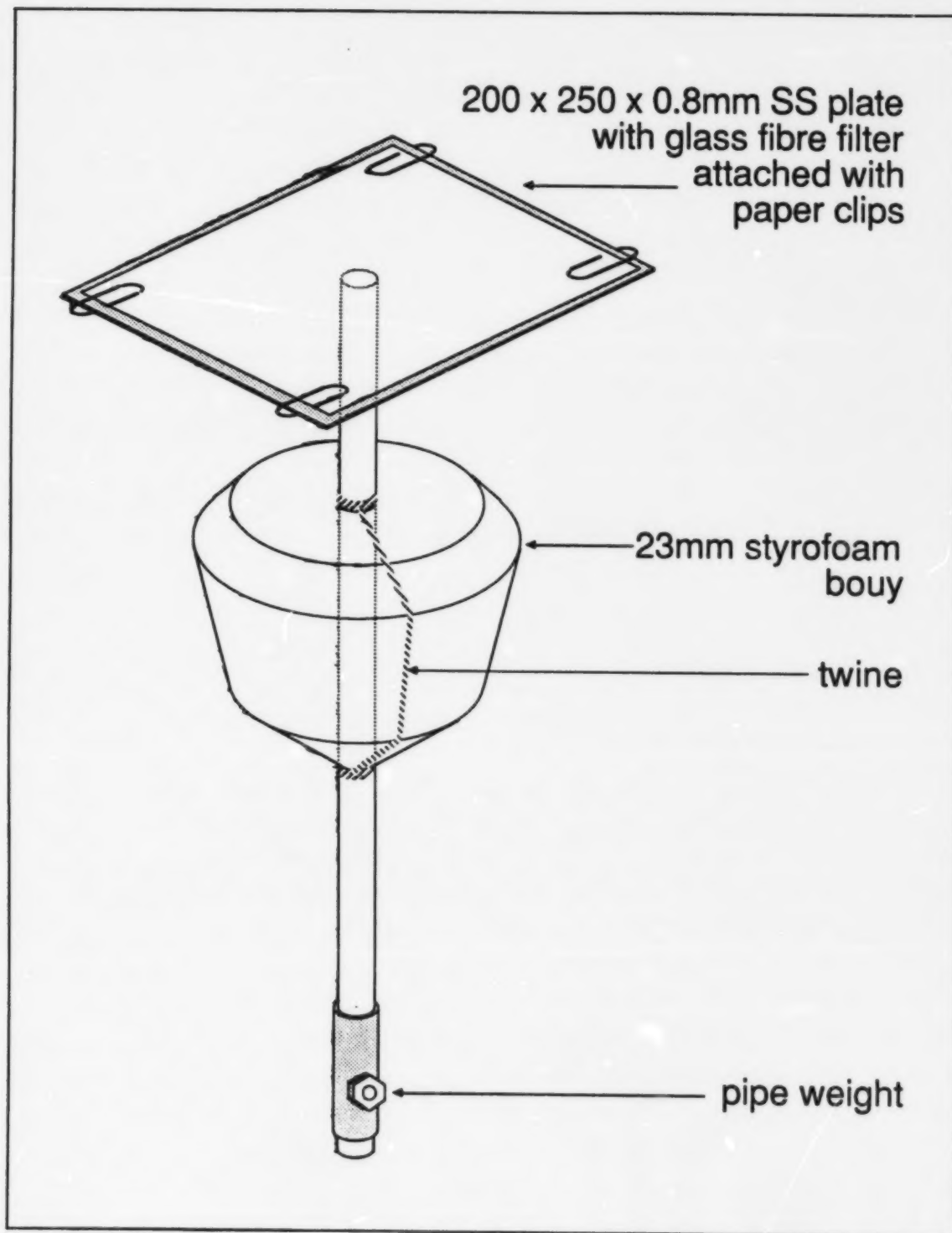


FIGURE 5 FLOATING FLAT PLATE SAMPLERS USED TO COLLECT SPRAY DEPOSIT

rinsed with distilled water/hexane. Samples were obtained by immersing the bottles such that one edge of the lip was approximately 1 cm below the surface. In this way, only the top 0-1 cm of water was sampled. Water sample extraction was begun immediately in the field by adding 150 mL of hexane and shaking vigorously for 5 min. After the samples had been treated in this way, they were placed in coolers and transported to a laboratory in Charlottetown, where they were fully extracted within 12 h of sampling.

2.5.4 Benthic Invertebrates

One month prior to spray, approximately 50 artificial substrates were deployed in each pond. This has been demonstrated to be a sufficient period of time to allow for total colonization by endemic benthic invertebrates (Coleman and Hynes, 1970). The artificial substrates (Fig. 6) consisted of 12 8 cm x 8 cm x 3 mm masonite boards, separated by spacers of the same masonite material, weighted on one end by two iron bars which were fastened with a 15 cm ring bolt. To facilitate locating the artificial substrates, a small wooden float was attached to the sampler by light twine.

The substrates were distributed in shallow water (less than 1 m) at the predominant windward end of each pond. Prior to spray and at seven intervals throughout the summer, three to six of the samplers were randomly retrieved by placing an 800 um wet sediment sieve under the sampler and gently lifting it from the water. The sampler was dismantled in the sieve and placed with the contents of the sieve in a 1-L plastic container with enough isopropanol to cover the plates. All of the invertebrates so collected were subsequently sorted to the lowest convenient taxa and enumerated. The intent of these measurements was to determine the spray impacts on benthic invertebrates.

Aquatic fauna were also held alive in cages for observation at various times after spray. Holding cages (Fig. 7) consisted of sleeves of

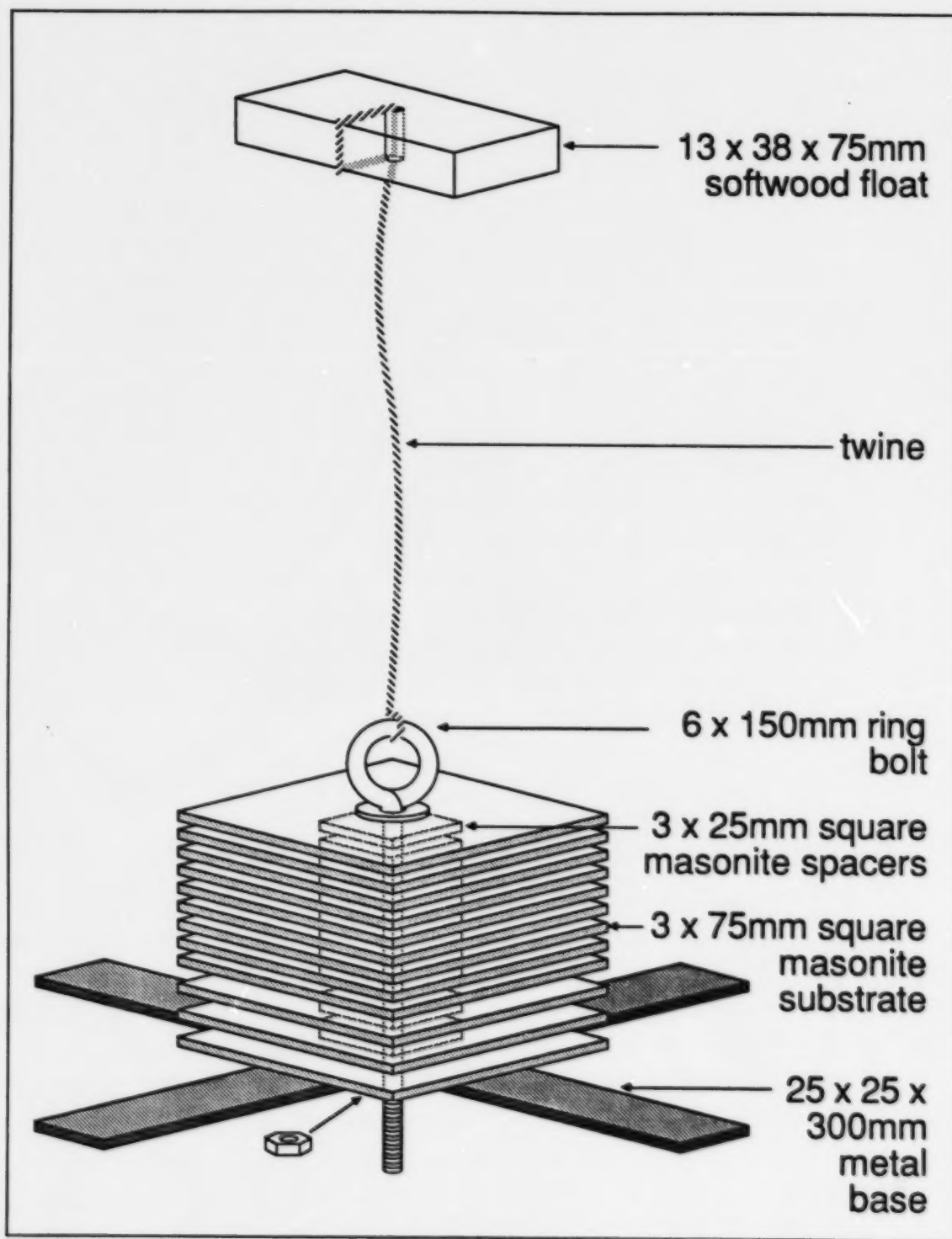


FIGURE 6 ARTIFICIAL SUBSTRATE SAMPLERS USED TO DETERMINE BENTHIC INVERTEBRATE ABUNDANCE IN STUDY PONDS

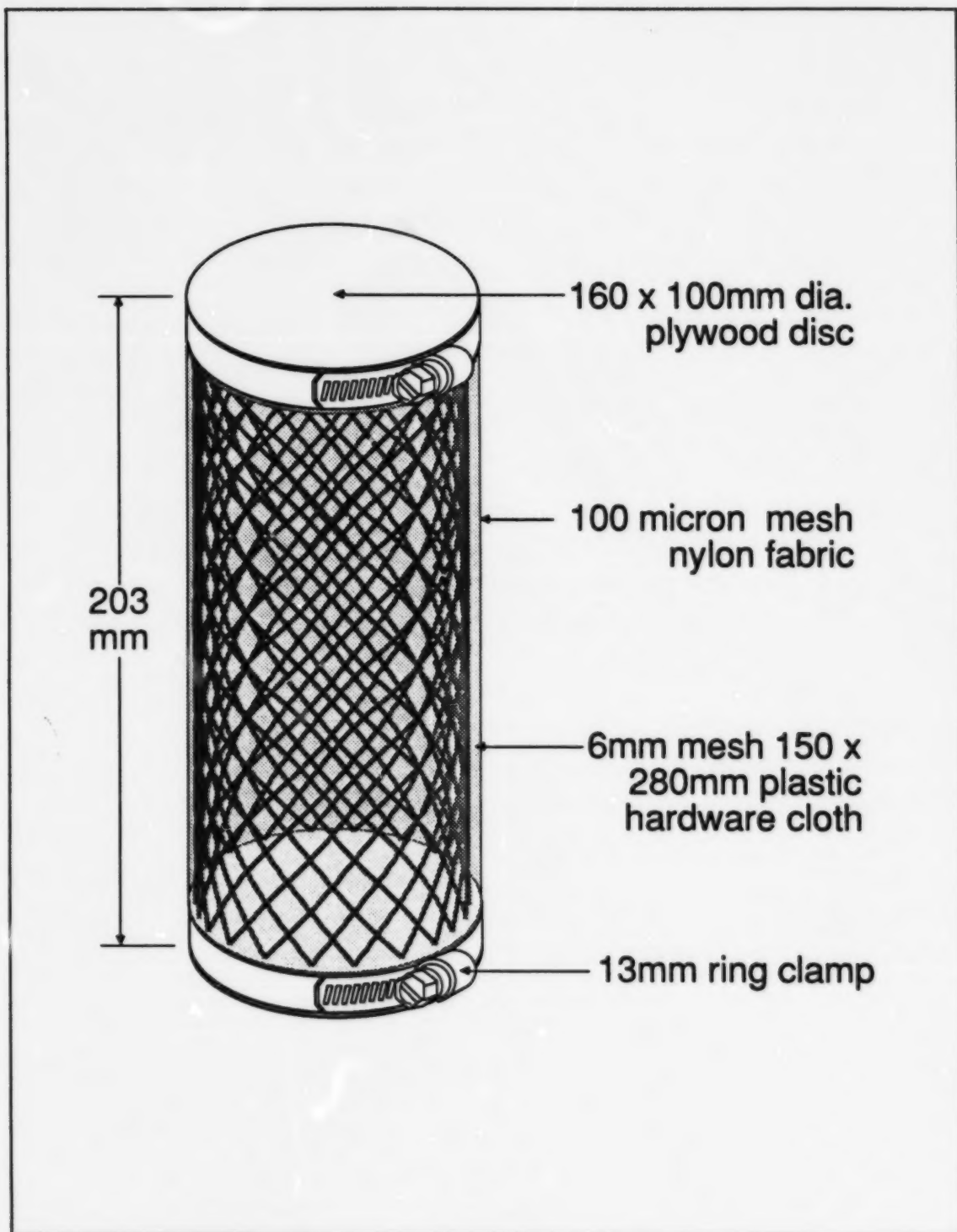


FIGURE 7 CAGES USED TO HOLD LIVE INVERTEBRATES IN STUDY PONDS

nylon fabric (100-um mesh) 20-cm in length clamped to 10-cm diameter circular pieces of plywood. Rigidity was provided by a piece of polyurethane hardware cloth coiled inside the nylon sleeve. One day prior to the first spray, a number of different taxa of pond fauna were captured in the overspray treatment pond with a dip net and placed in cages. In most instances, approximately 10 individuals were placed in each cage, however, for certain cannibalistic species such as Aeshna sp. each individual was housed in a separate cage. Animals placed in cages included: caddis flies (Limnephilus psychoglypha); water boatmen (Sigara mehesoni); dragonflies and damsel files (Aeshna sp.); midges (Chironimidae); diving beetles (Colymbetes sculptilis); mites (Acarina); snails (Stagnicola elodes); and stickleback (Gasterosteus aculeatus). Cages were then distributed throughout the pond, adjacent to the deposit samplers.

For the second treatment at the overspray site only the animals which were particularly sensitive to the first spray effects, caddis flies, water boatmen and stickleback, were placed in cages and observed. These animals were obtained from an adjacent pond. For the final treatment at the oversprayed pond, animals which were again collected from an adjacent pond were placed in live cages at various times after spray in an effort to determine the duration of lethal effects.

In the pond which was protected by the 100-m set-back, caddis flies and water boatmen only were placed in cages and observed at various times after spray.

Yearling brook trout (Salvelinus fontinalis) were obtained from the Cardigan, P.E.I. fish hatchery and placed in holding cages in each of the ponds prior to spray. Approximately 5 fish were placed in each cage. Cages consisted of wooden frames which were covered by nylon netting (0.5 cm mesh) equipped with a hinged top for ease of observation. The cages, which measured 50 cm x 37 cm x 29 cm, were slightly positively buoyant.

3.0 RESULTS

3.1 Subsurface Water - Pond

(1+1')-Deltamethrin disappeared quickly from bulk subsurface water as shown in Fig. 8. A maximal concentration of 320 ng/L was reached 0.7 h after the spray and the concentration declined with a half-life of about 1 h. The concentration declined to 1% of its initial maximum after 1 d and measurable concentrations were still found 2-3 d after the spray. Table 3 shows the concentrations of the parent (1+1')-deltamethrin as well as those of the transformation and degradation products detected. The less toxic (2+2')-deltamethrin was the only isomer found. Its concentration never exceeded 14 ng/L but over 2-3 d it became a major contributor to the total deltamethrin concentration. The concentration of the (2+2') isomer was up to 70% of that of the (1+1') isomer. DBCA, PBald, PBalc and PBacid were all detected occasionally, sometimes at concentrations which exceeded the (1+1')-deltamethrin. However, the total concentration of the deltamethrin isomers and the four degradation products mentioned declined quickly, with only approximately 10% of the original deltamethrin accounted for after 24 h.

Table 4 demonstrates that (1+1')-deltamethrin was found in both suspended solids and dissolved phases, but in general exhibited no pronounced preference for either phase. These results agree with those of Muir et al. (1985) on total deltamethrin. The same was true of (2+2')-deltamethrin. By contrast, the four degradation products were only found in the suspended solids phase. Table 5 shows that the apparent suspended solids-to-water partition coefficients of the (1+1') and (2+2') isomers of deltamethrin were fairly constant with time after the spray. Similar results to those in Tables 4 and 5 were obtained for deltamethrin in stream water at Site B. These observations agree with a prediction made using an octanol-water partition coefficient (K_{ow}) of 2.5×10^6 (Briggs et al. 1983) and Karickhoff's (1981) regression equation:

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346$$

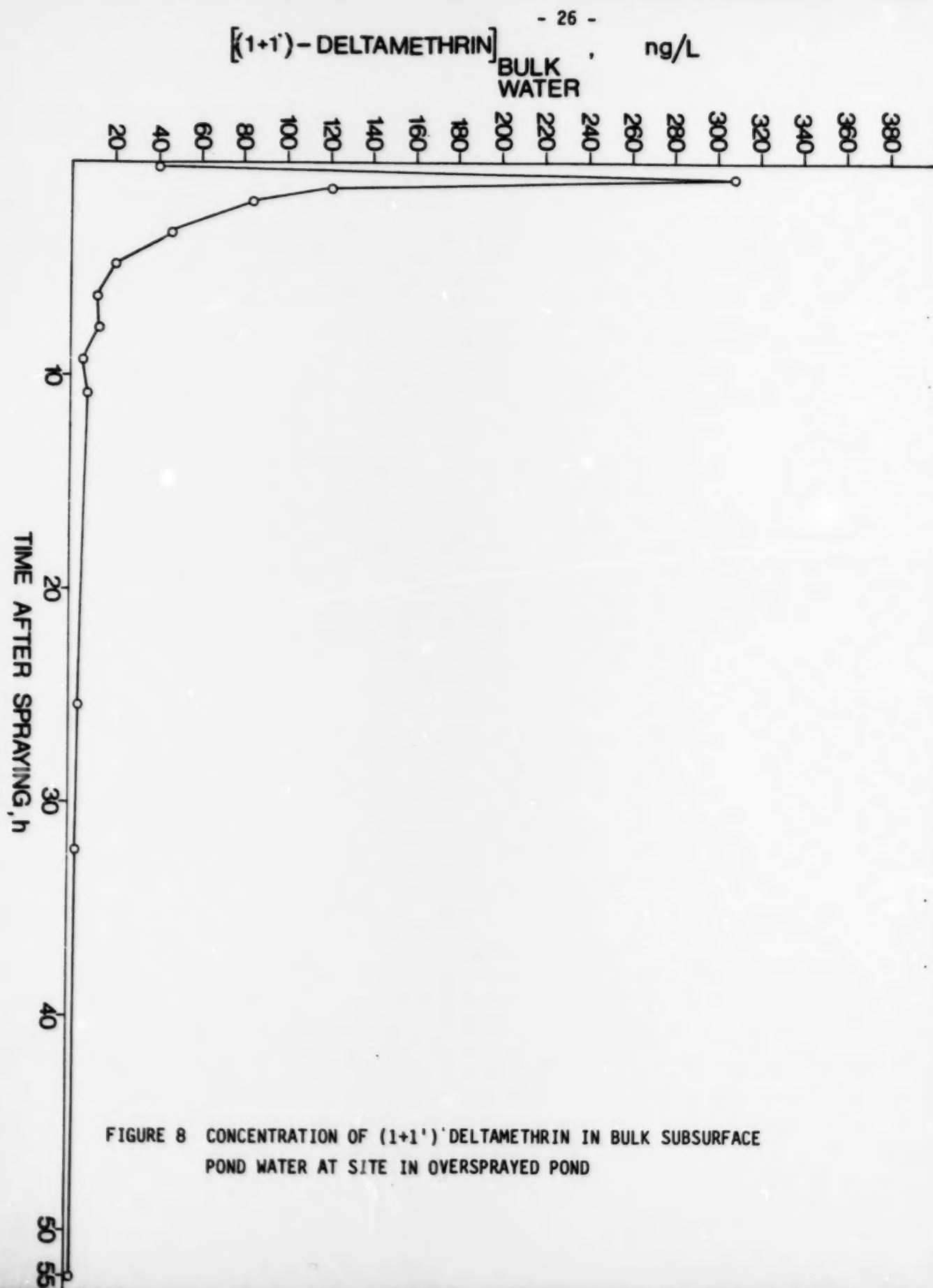


FIGURE 8 CONCENTRATION OF (1+1')-DELTAMETHRIN IN BULK SUBSURFACE POND WATER AT SITE IN OVERSPRAYED POND

TABLE 3 - CONCENTRATIONS (ng/L) OF DELTAMETHRIN AND TRANSFORMATION PRODUCTS IN BULK SUBSURFACE POND WATER AFTER DIRECT OVERSPRAY

Time, (h)	[(1+1')]	[(2+2')]	[DBCA]	[PBald]	[PBalc]	[PBacid]	[Total] mol/L at t=0.7h x 10 ¹⁰	[% Total]
0.2	41.1	0.6	9.0				1.13	
0.7	308.0	14.2	3.6				6.70	100.0
1.2	120.0	7.3		0.6	2.4		1.13	17.2
1.7	83.4	8.6		1.9	7.5	6.2	1.99	30.0
3.2	45.8	11.7	6.8				1.37	20.0
4.7	20.1	6.4	6.6				0.75	11.0
6.2	11.4	4.9	2.7				0.41	6.0
7.7	11.9	5.9					0.35	5.0
9.2	52.9	2.8					1.16	17.0
10.7	7.2	2.8				0.9	0.47	7.0
25.4	3.9	2.7		0.6	3.5		0.13	2.0
32	3.3	1.2					0.69	10.0
55	2.0	1.2				10.0		0.0
271								

**TABLE 4 - DISTRIBUTION OF (1+1')-DELTAMETHRIN IN POND WATER BETWEEN
DISSOLVED PHASE AND SUSPENDED SOLIDS**

Time after spray (h)	% dissolved	% with suspended solids
-------------------------	-------------	-------------------------

0.2	71	29
0.7	41	59
1.2	63	37
1.7	47	53
3.2	68	32
4.7	36	64
6.2	25	75
7.7	24	76
9.2	92	8
10.7	97	3
25.4	65	35
32	55	45
55	38	62

TABLE 5 - APPARENT SUSPENDED SOLIDS-TO-WATER PARTITION COEFFICIENTS OF DELTAMETHRIN ISOMERS AS A FUNCTION OF TIME AFTER SPRAY

Time (h)	K _p apparent (1+1')	K _p apparent (2+2')
0.2	8.11 x 10 ⁴	
0.7	1.76 x 10 ⁵	2.04 x 10 ⁵
1.2	9.34 x 10 ⁴	1.36 x 10 ⁵
1.7	2.44 x 10 ⁵	2.19 x 10 ⁵
3.2	7.06 x 10 ⁴	4.38 x 10 ⁴
4.7	4.06 x 10 ⁵	3.52 x 10 ⁵
6.2	2.99 x 10 ⁵	2.87 x 10 ⁵
7.7	3.08 x 10 ⁵	3.43 x 10 ⁵
25.4	1.63 x 10 ⁵	3.39 x 10 ⁵
average $\pm$	(2.05 $\pm$ 1.17)x10 ⁵	(2.40 $\pm$ 1.11)x10 ⁵

K_p = (ug/kg in suspended solids) / (ug/L in dissolved phase)

In this equation K_{OC} is the organic carbon normalized partition coefficient, equal to the suspended solids-to-water partition coefficient (K_p of Table 5) divided by the fractional organic carbon content of suspended solids, usually assumed to be 0.1. This prediction also employed a suspended solids concentration in pond water of 10 mg/L, which is the average of 14 determinations from the oversprayed ponds.

It is possible to produce (2+2')-deltamethrin from (1+1')-deltamethrin by photochemical and dark chemical reactions (Ruzo et al. 1977; Hill and Johnson 1987). Experiments conducted in the laboratory with (1+1')-deltamethrin formulations injected below the surface of sterile pond water showed the production of (2+2')-deltamethrin in water in the dark. Fig. 9 shows that even after a few hours in the dark the concentration of the (2+2')-deltamethrin isomer in water forms a significant percentage of the total isomer concentration. In these experiments the first half-life of disappearance of the parent (1+1')-deltamethrin was about 2 d. The rate of disappearance of (2+2')-deltamethrin was similar after it reached its maximal concentration 290 h after the experiment began. In neither case however, was the decline in isomer concentration exponential over several half-lives. It is possible that some of the deltamethrin volatilized (see below). No traces of either isomer were found after 35 d. Degradation products were not sought in these studies. These results indicate that small quantities of (2+2')-deltamethrin can be produced between the time an emulsifiable concentrate of deltamethrin is mixed with water and the time it is applied.

3.2 Subsurface Water - Stream

The concentration of (1+1')-deltamethrin declined slightly faster at Site B in the stream than in the pond. The results are shown in Table 6. A maximal concentration of 220 ng/L was reached 0.7 h after the spray and the concentration declined with a first half-life of about 0.5 h. The concentration declined to about 1% of its initial maximum after 1 d but low

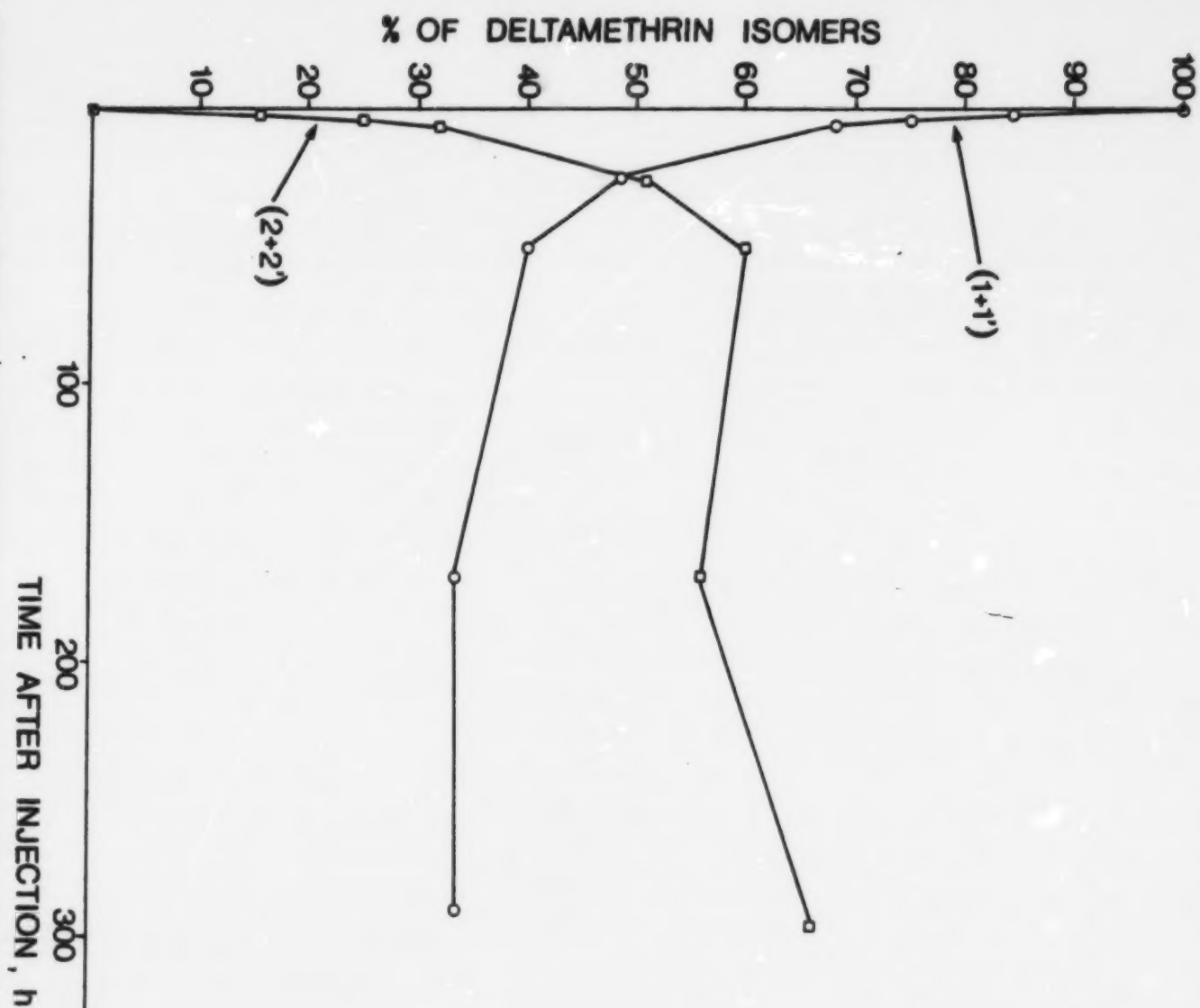


FIGURE 9 PERCENTAGE OF DELTAMETHRIN ISOMERS IN STERILE POND WATER IN THE DARK AFTER INJECTION

**TABLE 6 - CONCENTRATIONS (ng/L) OF DELTAMETHRIN ISOMERS
AND TRANSFORMATION PRODUCTS IN BULK STREAM WATER
AT SITE B AFTER THE SPRAY**

Time (h)	[(1+1')]	[(2+2')]	[DBCA]	[PBald]	[PBalc]
0.2	171.0	2.0	11.2		
0.7	218.0	84.1	9.8		
1.2	95.6	2.8	4.2	0.5	
1.7	43.2	2.4	7.0		
3.2	31.0	2.5	2.5	1.0	2.9
4.7	17.1	3.4	6.0		
6.2	9.5	3.1		0.6	2.0
7.7	4.4	1.2			
10.7	15.7	3.9	12.4		
25.4	1.5	3.3	2.9		
32	3.1	0.6	2.5		
55	0.3		2.6		
94	0.4		3.3		
122	0.5	0.5	3.0		
123	0.4		2.3		
124	0.6		2.7		
125	0.5	0.9	3.2		
126	0.1				
127	0.6				
269	0.9	0.1			

concentrations were found as long as 11 d post-spray, possibly due to the transport of field-derived runoff in small tributaries to the stream.

As in the case of pond water, (2+2')-deltamethrin, DBCA, PBald and PBalc were detected, but not PBacid. DBCA and (2+2')-deltamethrin in particular were consistently detected and after the first few hours these chemicals formed a significant part (up to 70% and 20% respectively) of the total amount of all compounds detected. A mass balance as a function of time was not calculated in Table 6 since it would not be realistic for a flowing system.

Table 7 shows the concentrations of (1+1')-deltamethrin and the only other chemicals detected in bulk subsurface water at Site D which was 2 km downstream of the spray. The water transit time was estimated earlier to be about 2 h. The concentration of (1+1')-deltamethrin reached a maximum of 32 ng/L 6.5 h after the spray and declined to 1 ng/L, or less, within 3 d. The concentration of (2+2') isomer was usually less than 1 ng/L and accounted for little of the total concentration of deltamethrin isomers for the first 24 h after the spray. PBacid was observed only twice, and only in the suspended solids phase. No other transformation or degradation products were detected.

3.3 Surface Microlayer - Pond

The initial concentration of (1+1')-deltamethrin (approximately 50 ug/L) in the surface microlayer corresponded to roughly 30% of the deposit estimated by exposed glass fibre filters 30 cm above the surface of the water (see Table 10, Section 3.5), which is itself about 34% to 44% of the emitted dose of 6.2 g ai/ha. As shown in Table 8, (1+1')-Deltamethrin disappeared very quickly from the surface microlayer. The half-life was about 5 min, and although less than 1% of the initial deposit remained after 5 h, there was still a notable concentration (42 ng/L) 55 h after the spray. Large concentrations of (2+2')-deltamethrin were also found shortly

TABLE 7 - CONCENTRATIONS (ng/L) OF DELTAMETHRIN ISOMERS AND PBacid IN
BULK STREAM WATER 2 km DOWNSTREAM OF SPRAY AT SITE D

Time (h)	[(1+1')]	[(2+2')]	[PBacid]
1.9	7.6		
2.9	9.5	0.3	
3.9	11.5	0.5	
4.9	26.3	0.5	
6.4	32.0	0.6	
7.9	12.9	0.2	
9.4	9.2		
10.9	7.4	1.2	
25.9	4.8	0.2	
31	4.2	0.7	2.6
54	0.9	0.2	2.3

TABLE 8 - CONCENTRATIONS (ng/L) OF DELTAMETHRIN ISOMERS AND TRANSFORMATION PRODUCTS IN BULK SURFACE MICROLAYER OF THE POND AT SITE A AFTER THE SPRAY

Time (h)	[(1+1')]	[(2+2')]	[PBald]	[PBalc]	[Total] mol/L $\times 10^7$	% of [Total] at t = 0.1 h
0.1	49400	6110	61.9	67.2	1.11	100.0
0.3	19300	804	50.7		0.41	36.0
0.4	2970	91.8	19.1		0.06	5.0
0.6	1690	89.0	7.7		0.04	3.0
0.7	862	95.8	6.6		0.02	2.0
0.9	720	80.0			0.02	2.0
1.7	368	40.9	10.3		0.01	1.0
3.3	680	75.5			0.02	2.0
4.2	595	73.6			0.01	1.0
4.8	229	57.2	7.2		0.01	1.0
6.4	80.8	20.2				
7.8	99.2	24.8				
9.3	203	41.5				
10.7	69.3	20.7				
26	14.6	9.4				
32						
55	42.3	8.7				

after the spray and, as discussed above, may have been produced in the spray tanks after the emulsifiable concentrate was mixed with water. The concentration of (2+2')-deltamethrin also declined quickly. PBald was detected frequently, PBalc only once and no other product was detected.

Attempts to demonstrate the significance of volatilization of (1+1')-deltamethrin from the surfaces of sterile pond water in the laboratory were complicated by the production of significant concentrations of (2+2')-deltamethrin. Nevertheless, the half-life of disappearance of (1+1')-deltramethrin from the whole volume of water after spraying on the surface was 2-3 h, compared with 2 d if deltamethrin was injected below the surface, as shown in Figure 10. The half-life of disappearance of (1+1')-deltamethrin from subsurface water in these laboratory experiments (2 d) was much greater than that observed in subsurface water in the pond (1 h), probably because of the absence of photolysis, biological degradation, and adsorptive sediment in the laboratory experiments. Rates of disappearance of deltamethrin were similar, whether azide-poisoned pond water or organic-free water were used.

As noted above, the (3+3') and (4+4') isomers of deltamethrin, as well as the (2+2') isomer, can be produced by the action of sunlight on (1+1')-deltamethrin. No (3+3') or (4+4') isomers were detected in any of the laboratory experiments or in any water or sediment sample.

3.4 Sediment - Pond

Table 9 shows that the (1+1') and (2+2') isomers were only infrequently detected in pond sediment. DBCA, however, was found in high concentrations relative to that of total deltamethrin, reaching a maximum of 0.4 mg/kg dry weight 3 h after the spray. PBald and PBalc were found at concentrations comparable to those of the deltamethrin isomers. No trace of deltamethrin isomers or degradation products was found in pond sediment 1 d after the spray.

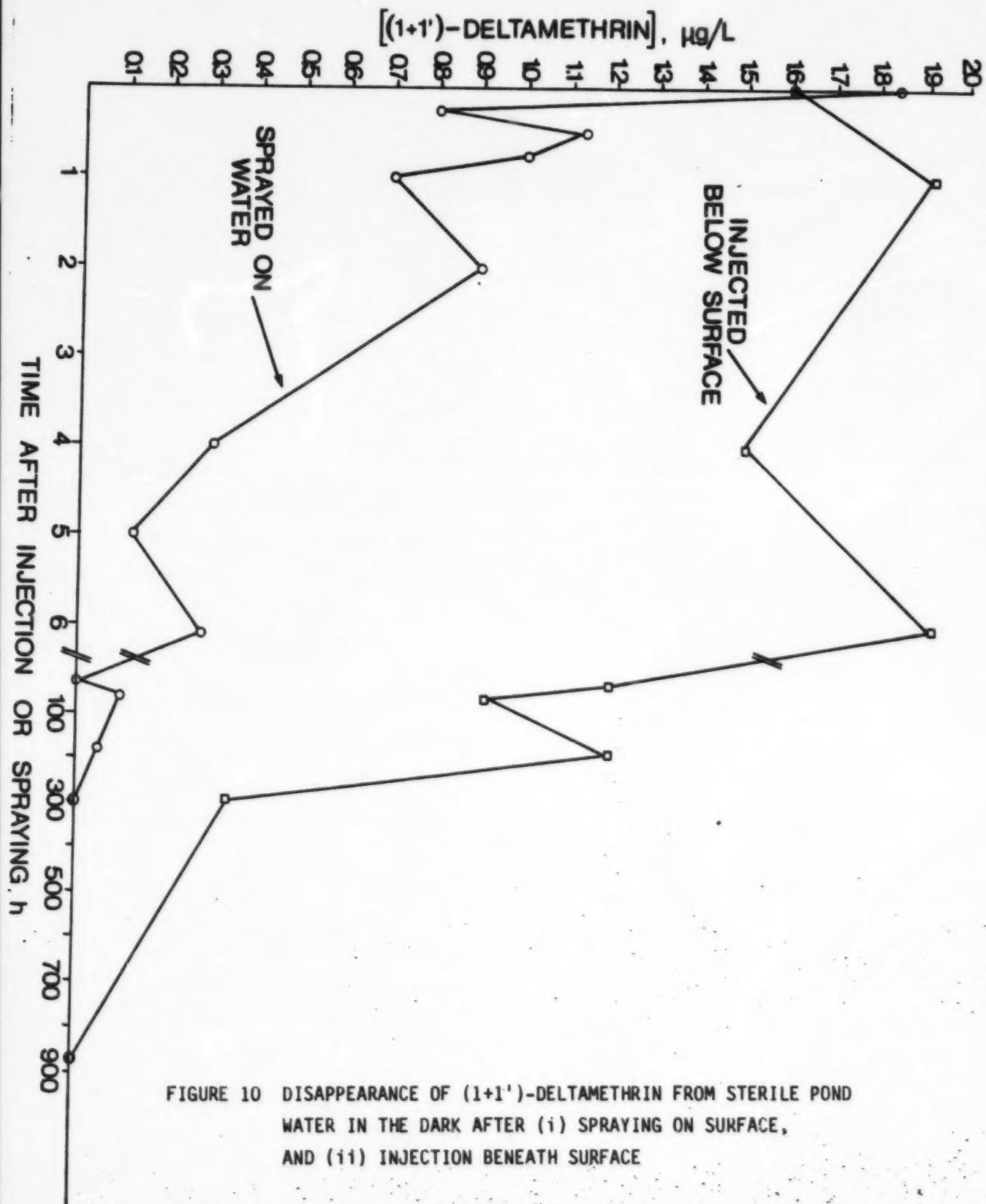


FIGURE 10 DISAPPEARANCE OF (1+1')-DELTA METHRIN FROM STERILE POND WATER IN THE DARK AFTER (i) SPRAYING ON SURFACE, AND (ii) INJECTION BENEATH SURFACE

**TABLE 9 - CONCENTRATIONS (ug/kg dry weight) OF DELTAMETHRIN ISOMERS
AND TRANSFORMATION PRODUCTS IN TOP 2 cm OF POND SEDIMENT
AT SITE A AFTER THE SPRAY**

Time (h)	[(1+1')]	[(2+2')]	[DBCA]	[PBa1d]	[PBa1c]
0.2					
0.7			56.6	3.8	
1.2	11.2	1.8		9.7	20.3
1.7				2.5	
3.2			429.2		
4.7			240.6		
6.2			158.4		
7.7			315.8		
9.2			132.8		
10.7	7.3	1.7			
25.4	8.1	0.9			
32					
55					

3.5 Buffer Zone Effectiveness

The combined results of deltamethrin deposits on each of the ponds are shown in Table 10. The values presented in Table 10 represent a combination of the parent deltamethrin and (2+2')-deltamethrin (subsequently identified by G.C./M.S.). The deposits on the oversprayed pond were somewhat variable, mean measured deposit for individual spray events ranging from 188 to 245 ug/m². The mean deposits on the oversprayed pond represented a range of 34% to 44% of the emitted dose. The maximum mean deposit of deltamethrin on the filter papers in the set-back pond was less than 0.5% of the mean deposits measured in the overspray situation. The maximum mean deposit (July 16) was only 0.2% of the emitted dose. After the August 13th spray event, during which wind conditions were very light (3.6 km/h) the deltamethrin content of exposed filter paper was below the detection limit of the analytical procedure.

The surface water concentrations of deltamethrin at 15 min post-spray in the oversprayed pond were variable, but all were above the analytical detection limit. The mean deltamethrin concentration, for individual spray events, ranged from 2.2 ug/L to 11.9 ug/L (Table 10). The highest deltamethrin concentration was 24 ug/L. Much of the deltamethrin was probably lost from the surface top 1 cm by the time of sampling since the values recovered from water samples represented 1/2 to 1/8 of the amount deposited on the collectors. Table 10 indicates that most of the surface concentrations of deltamethrin in the set-back pond were low. In about one third of these samples there were no residues above the detection limit.

Combining the results of the three spray events for each pond, the net effect of the 100 m set-back, under the observed conditions, was to reduce the measured surface water concentration to approximately 1/145, and to reduce the mean measured deposit to approximately 1/450 of that measured on the oversprayed ponds.

TABLE 10 - EFFECTIVENESS OF 100 METRE BUFFER ZONE IN REDUCING
DELTAMETHRIN DEPOSIT ON POND

Pond	Spray Event	Deposit ^a	
		Filter paper (ug/m ²)	Surface water (ug/L)
Oversprayed	1	245 ± 85	3.3 ± 7.1
	2	241 ± 75	11.9 ± 8.1
	3	188 ± 141	2.2 ± 3.1
	Total	225 ± 104	5.8 ± 7.6
Set-back	1	1.1 ± 0.56	0.05 ± 0.07
	2	L ^b 0.1	0.01 ± 0.02
	3	0.60 ± 0.30	0.05 ± 0.04
	Total	0.54 ± 0.57	0.04 ± 0.05
Reduction due to set-back		1/140	1/145

a presented as mean ± 1.s.d.

b L = less than

The visible impact on the resident fauna of the oversprayed pond after the first spray event was significant. Within approximately 5 min post treatment, many invertebrates began to surface in a distressed condition. The most rapidly affected were the surface dwelling organisms such as water boatmen and gyrenids; however within several hours of spray, bottom dwelling limnophilids were seen dead in large numbers. Dead and dying invertebrates collected in windrows on the margins of the pond. No dead or distressed native fish were observed after the spray. The visible impacts were less notable with each subsequent treatment at the oversprayed site. Since deposits were not substantially different for each spray event it is likely that the reduced impact with each subsequent spray was due to reduced numbers of organisms in the pond.

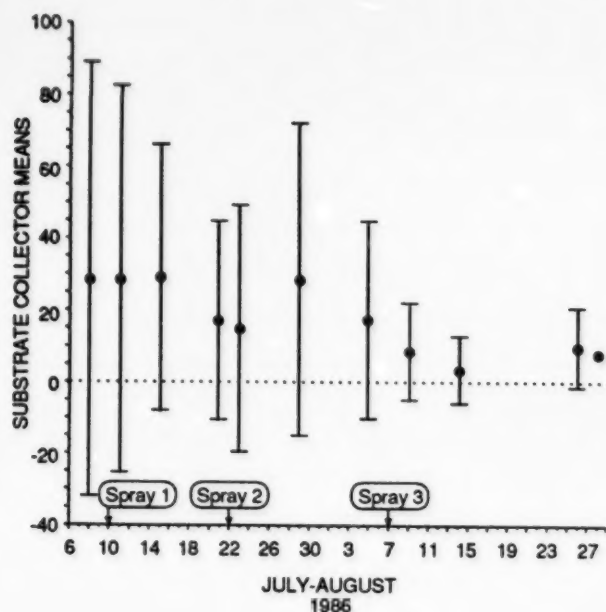
There was no visible effect associated with any of the three sprays on resident invertebrates at the site which was protected by the buffer zone.

Figure 11 presents the mean ($\pm$ S.D.) of total numbers of aquatic invertebrates populating artificial substrate collectors removed from the oversprayed pond. Figure 11 illustrates a general decrease in total numbers of invertebrates, up to the last sampling period.

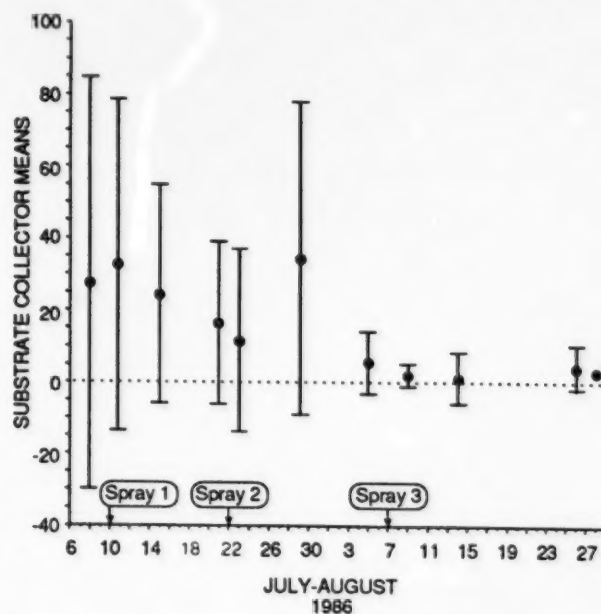
The total numbers of invertebrates on samplers in the set-back pond (Fig. 11), on the other hand, did not decline throughout the summer. This implies that the decline in total numbers at the oversprayed pond was not due to natural temporal changes such as loss due to emergence, but was associated with pesticide treatment.

The most dramatic decrease in invertebrate numbers at the oversprayed pond was for the chironomids (Fig. 11). That taxa declined from approximately 27 individuals per collector prior to the first spray to only 1 individual per collector after the final spray. Chironomid numbers in the set-back pond, on the other hand (Fig. 11) remained relatively constant throughout the summer.

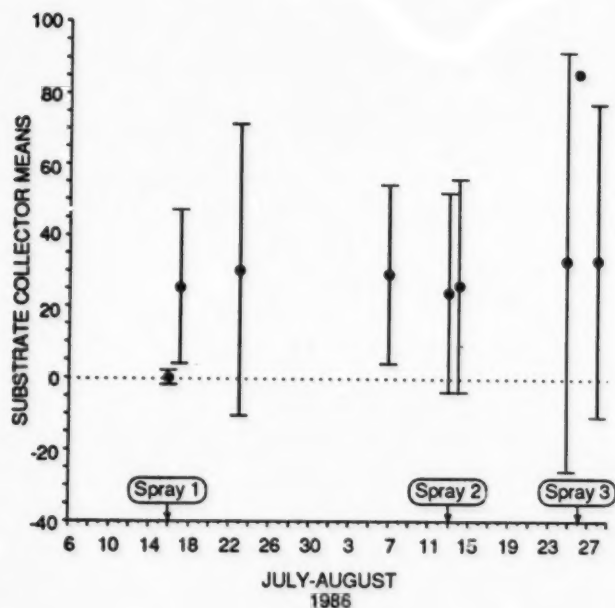
TOTAL INVERTEBRATES OVERSPRAYED



CHIRONOMIDS OVERSPRAYED



TOTAL INVERTEBRATES SET-BACK



CHIRONOMIDS SET-BACK

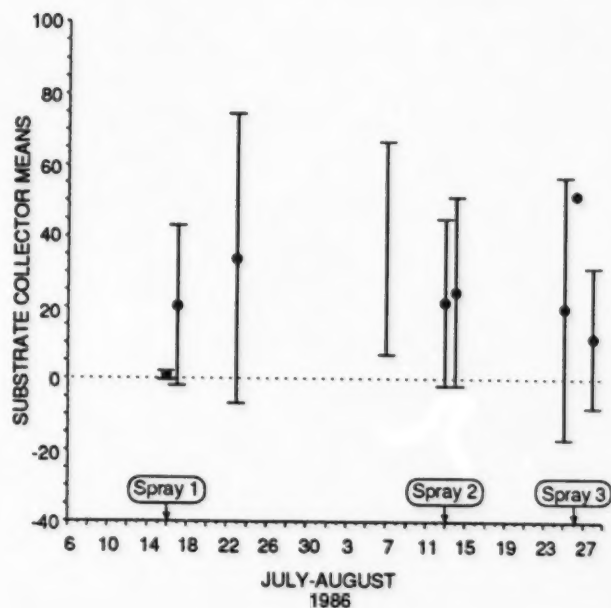


FIGURE 11 MEAN TOTAL NUMBER ($\pm$ 1 S.D.) OF AQUATIC INVERTEBRATES AND MEAN TOTAL CHIRONOMIDS COLONIZING ARTIFICIAL SUBSTRATES IN STUDY PONDS

The survival of caged fauna for the first two spray events at the oversprayed pond are presented in Table 11. All of the caged animals in the oversprayed pond suffered some level of mortality. The most rapidly affected were the water boatmen, chironomids and mites. Stickleback mortality was 80% in the stream but only 30% in the pond. Dragon flies, snails and caddisflies were the organisms which suffered the least mortality.

Caged invertebrates in the set-back pond suffered little or no mortality (Table 12). The highest mortality recorded (28%) was for water boatmen after the second spray, which had the least amount of pesticide deposit and lowest water concentrations. These mortalities are more likely due to handling than to spray effects.

When water boatmen were placed in holding cages at various times after direct spray, it was observed that surface pond water lost its toxic effect with time (Fig. 12). This process was surprisingly slow, however, and water boatmen which were placed in cages at 13 h post-spray suffered 35% mortality up to 25 h post-spray.

Thirty percent of the brook trout held in surface cages in the oversprayed pond had died by the termination of the study (Fig. 13). No trout mortality occurred in the set-back pond. Since water quality characteristics were very similar in these ponds and handling procedures were the same, the difference in mortality rates can only be attributed to differences in pesticide exposure.

TABLE 11 - SURVIVAL OF CAGED INSECTS IN OVERSPRAYED POND

Spray event	Insect taxa	Total n	Percent survival (post spray intervals)			
			2 h	7 h	12 h	23 h
1	Trichoptera					
	<u>Limnephila</u>	80	100	84.6	79.2	20
	<u>psychoglypha</u>					
	Hemiptera	80	0	0	0	0
	<u>Sigara</u>					
	<u>mehesoni</u>					
	Odonata	15	73.3	60	46	-
	<u>Aeshna</u> sp.					
	Pulmonata*	20	50	50	50	35.3
	<u>Stagnicola elodes</u>					
	<u>Gasterosteus</u>					
	<u>aculeatus*</u>	10	20	20	20	20
	Diptera					
	Chironimidae*	10	0	0	0	0
2	Acarina*	10	0	0	0	0
	Coleoptera					
	<u>Colymbetes</u>	2	0	0	0	0
	<u>sculptilis</u>					
			4 h	9 h	24 h	
	Trichoptera					
	<u>Limnephila</u>	90	83.3	76.3	60.6	
	<u>psychoglypha</u>					
	Hemiptera	108	1.9	0.9	0.9	
	<u>Sigara</u>					
	<u>mehesoni</u>					
	<u>Gasterosteus</u>					
	<u>aculeatus</u>	98	78.6	75.5	69.7	

*Cages in Stream

TABLE 12 - SURVIVAL OF CAGED INSECTS IN SETBACK POND

Spray event	Insect taxa	Total n	Percent survival (post spray intervals)			
			3 h	5 h	8 h	24 h
1	Trichoptera					
	<u>Limnephila</u>	50	100.0	100.0		
	<u>psychoglypha</u>					
	Hemiptera	50	100.0	100.0		
2	<u>Sigara</u>					
	<u>mehesoni</u>					
	Trichoptera					
	<u>Limnephila</u>	50	98.0	96.0	94.0	92.0
3	<u>psychoglypha</u>					
	Hemiptera	50	86.0	84.0	84.0	71.7
	<u>Sigara</u>					
	<u>mehesoni</u>					
3	Trichoptera					
	<u>Limnephila</u>	50	100.0	92.0		
	<u>psychoglypha</u>					
	Hemiptera	50	94.0	79.2		
	<u>Sigara</u>					
	<u>mehesoni</u>					

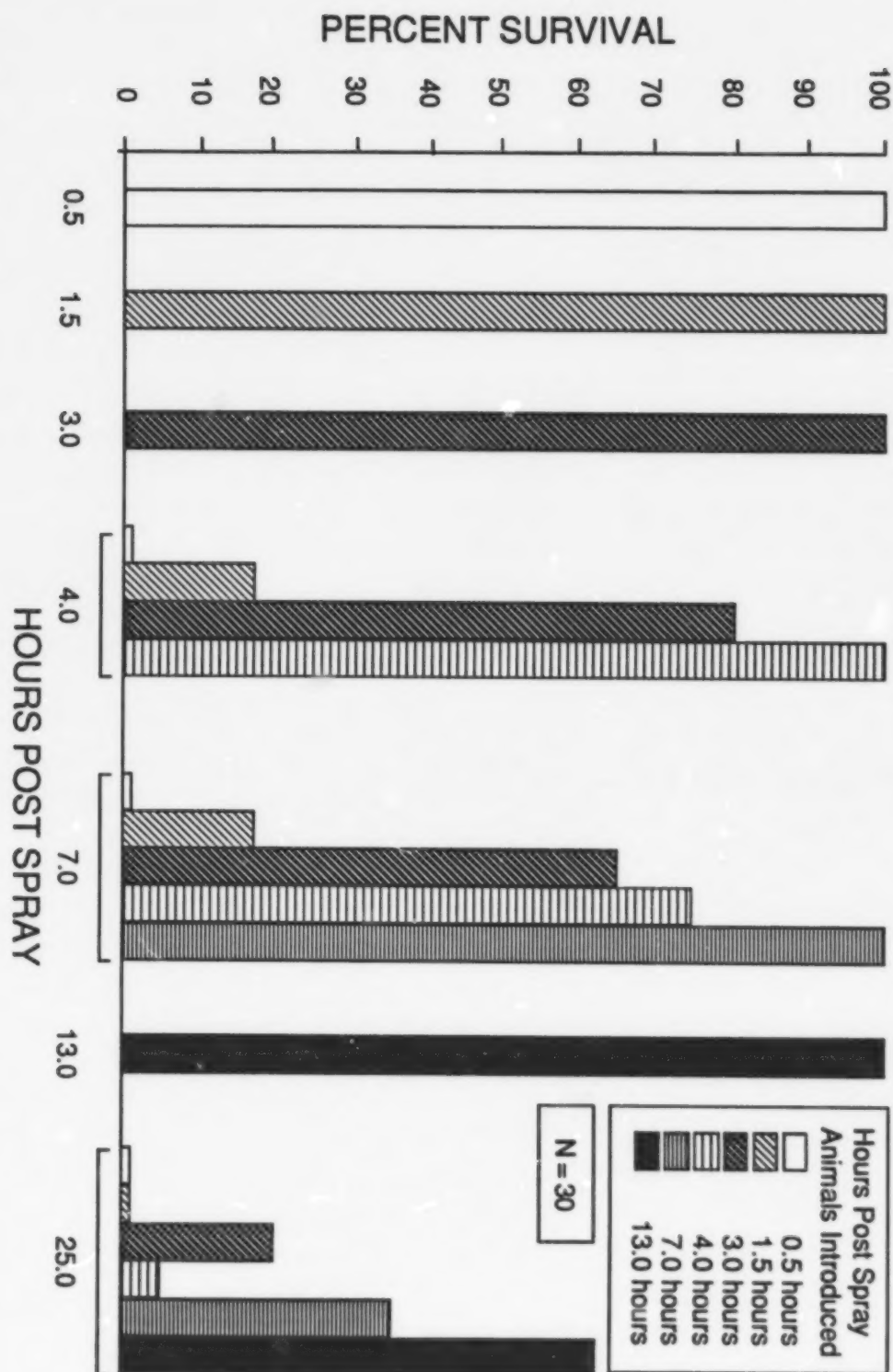


FIGURE 12 SURVIVAL OF CAGED WATER BOATMEN INTRODUCED TO OVERSPRAYED POND AT VARIOUS TIMES AFTER SPRAY

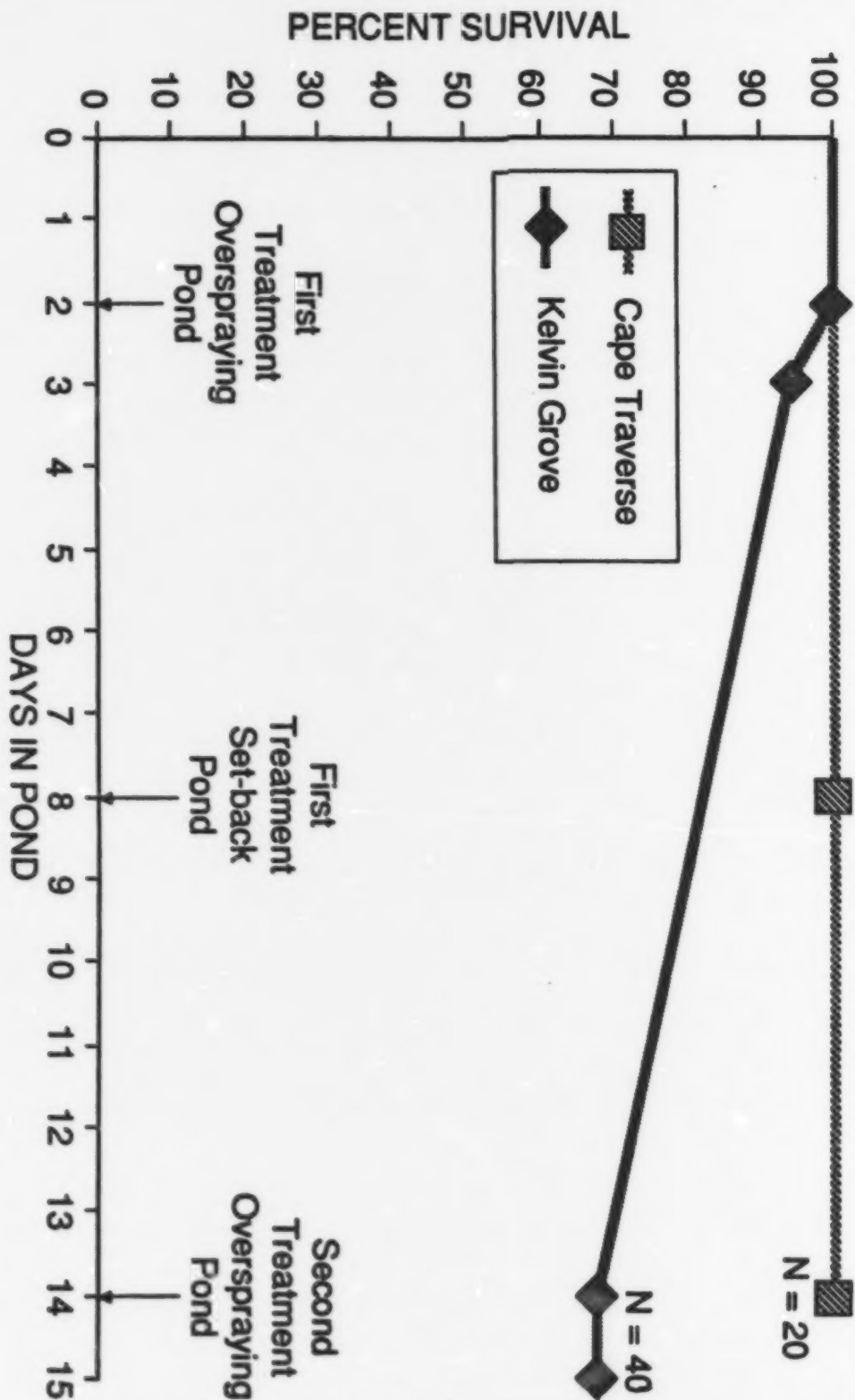


FIGURE 13 SURVIVAL OF CAGED BROOK TROUT IN STUDY PONDS

4.0 DISCUSSION

The results of this study confirm the rapid disappearance from subsurface water of total deltamethrin and (1+1')-deltamethrin in particular, which had a half-life of about 1 h. Despite the poor mass balance for deltamethrin isomers and the four degradation products sought, it was clear that the (2+2') isomer and the four degradation products were major products in the first few hours after the spray, and that (2+2')-deltamethrin formed a substantial part of total deltamethrin after that time. Although rapid partitioning of (1+1')-deltamethrin from water to sediment was expected, the sediment analyses yielded no consistent pattern of appearance or disappearance of deltamethrin or degradation products. No trace of any of these compounds was found 24 h post-spray. These results are in contrast to those of Muir et al. (1985), who found half-lives of 5-14 d for total deltamethrin in sediment and even observed deltamethrin residues in that matrix up to 306 d post treatment.

The significance of volatilization of deltamethrin from water as a pathway of dissipation depends to a large degree on its method of introduction to water. The Henry's Law constant for deltamethrin dissolved in water is 95 torr L mol⁻¹ (Muir et al. 1985), which indicates a compound of low-to-medium volatility from water (Smith et al. 1980). Muir et al. (1985) observed volatilization of deltamethrin from ponds after subsurface injection and estimated that volatilization losses were of the order of 6% over 2-4 d. Our laboratory results with sprayed vs. injected formulations showed clearly that deltamethrin disappeared far faster when sprayed on water than when injected subsurface. It is reasonable to assume that the kinetics of isomerization and degradation were similar in both sets of experiments. Therefore, we conclude that volatilization of deltamethrin from its formulation sprayed on the surface of water may be an order of magnitude faster than the rate of loss by the same route of deltamethrin introduced subsurface. We have made similar observations with regard to the insecticide fenitrothion sprayed on the surface of water as opposed to injected under the surface (Maguire and Hale 1980). A terrestrial

analogy of this proposed rapid volatilization from the surface microlayer is provided by Hill (1985) who demonstrated a much faster loss of deltamethrin from soil if it were boom-sprayed compared to pipet-applied. They postulated that the high water volumes with pipet application washed the deltamethrin into the soil and, with less surface loss, dissipation was reduced. It may be that volatilization from the surface microlayer is the most important removal process for deltamethrin which settles on it.

There was no effort made to determine deposit sampler efficiency in this study; however it has been previously demonstrated that flat plate collectors are effective spray deposit collectors (Ghassemi et al. 1982, Yates et al. 1978). Deposit of spray on the target is never 100% of the emitted material (Maybank et al. 1974). Using similar application techniques target deposits as high as 70% of the emitted spray have been measured (Maybank et al. 1976); however deposits can also be as low as 30% of emitted volume (Ware et al. 1971). The volumes which we recorded on flat plate collectors were within this range at the oversprayed site. The factors which may affect the on-site deposit of sprays and conversely the amount which is deposited off-target include: atmospheric turbulence; wind speed; droplet size distribution; formulation characteristics (Ghassemi et al. 1982); temperature; relative humidity (Maybank et al. 1976); release height; droplet density; and size of treated area (Warren 1976). The most important of these is turbulence and wind speed which, for the most part, were the only drift-controlling factors which were not uniform throughout all applications. The wind speeds recorded at the time of application to the set-back pond ranged from 3.6 to 11.2 km/h at a height of 10 m. This is a typical range of wind conditions expected during operational sprays and the upper limit exceeds the recommended upper limit of 8 km/h, thus representing a worst case situation. The fact that measured deposit on filter paper and in surface water was greatest at the set-back pond when wind speeds were greatest and least when wind speeds were lowest confirms the importance of wind speed as the major factor in off-target drift. The overall effectiveness of the 100 metre set-back is evidenced by the fact

that overall mean deposit on filter paper and concentration in surface water was reduced to 1/450 and 1/145 respectively in the set-back pond compared with the oversprayed pond. No explanation can be provided for the apparent difference in set-back effectiveness provided by the two methods of deposit measurement.

The effectiveness of the pond set-back was also evidenced by the difference in the magnitude of biological impact in the two ponds. The concentrations of deltamethrin deposited in the oversprayed pond were sufficient to cause mortality ranging from partial to total in all of the invertebrate species held in cages within 24 h of treatment. That mortality was due primarily to pesticide effects was evidenced by the fact that the initial residue concentrations of deltamethrin measured in the oversprayed pond were approximately 100 to 400 times the concentrations which have been shown to be lethal to aquatic invertebrates, such as a variety of species of mosquito larvae, in 24 h exposures (Rettich 1979). While invertebrate mortalities in the set-back pond were not as great as in the oversprayed pond, they may have been pesticide-induced since immediate post-spray deltamethrin concentrations were near the concentrations observed by Rettich (1979) to cause larval mosquito mortality. Caging stress cannot be ignored, however, as a possible effect contributing to mortality in this case.

In a study which compared the relative sensitivities of a number of different aquatic invertebrates to cypermethrin, it was observed that water mites (Piona carnea) were most sensitive, water boatmen (Corixa punctata) were least sensitive and midge larvae (Chironomus thummi, Chaoborus spp.) mosquito larvae (Aedes aegypti) and whirligig beetles (Gyrinus natator) were intermediate in sensitivity (Stephenson 1980). The concentrations of cypermethrin that were observed to be lethal during 2 h exposures in the Stephenson (1980) study ranged from 0.05 to 0.5 ug/L. It has been demonstrated that deltamethrin is the most toxic of the synthetic pyrethroid pesticides to aquatic fauna (NRCC 1986). Mean immediate post-spray water concentrations in the oversprayed pond were again from one

to two orders of magnitude greater than the above quoted values, while water concentrations in the set-back pond were very similar to them. In our study, the sensitivity differences of mites, chironomids and water boatmen could not be determined since 100% mortality of caged individuals of these species was usually complete within the first observation period (2 h post spray). The fact that boatmen, which were introduced to the pond 13 h after spraying, had 35% mortality within 25 h after spraying, is an indication that deltamethrin was persisting at lethal concentrations. As indicated in Table 8, most of the persisting deltamethrin measured in the pond at 25 h after spraying was in the surface microlayer.

It was surprising to observe mortality of caged snails since mollusc species are not generally sensitive to pyrethroid pesticides (NRCC 1986). There is evidence that deltamethrin may be somewhat different in this regard since shell growth in oysters (Crassostrea virginica) was reduced, compared with controls, in exposure concentrations of 1 to 32 ug/L (Lhoste and L'Hotellier 1982).

The fact that at the oversprayed site, caged stickleback suffered 20 to 80% immediate mortality while brook trout suffered 30% cumulative mortality throughout the 3-spray period is in keeping with the known toxicity of deltamethrin to fish. The measured 24 h LC50's for various fish species are closely grouped, ranging from 0.6 ug/L for the desert pupfish (Cyprinodon macularius) to 1.0 ug/L for the mosquitofish (Gambusia affinis)(Coats and O'Donnell-Jeffery 1979), with rainbow trout (Salmo gairdneri) being intermediate at 0.7 ug/L (Mulla et al. 1978). The mean surface water concentrations measured in the oversprayed pond ranged from twice to ten times these LC50 values. It has been shown that the presence of suspended solids in water can greatly reduce the bioavailability of pyrethroid pesticides (Reiff 1978 in NRCC 1986). This, plus dilution factors, would tend to ameliorate the deltamethrin toxicity in a pond situation. On the other hand, caging stress may have contributed to pesticide toxicity. Since there was no mortality of brook trout in the

set-back pond, however, it must be presumed that fish mortality in the oversprayed pond was due, in part, to pesticide exposure.

The artificial substrate sampling indicated a depletion in total numbers of benthic invertebrates after each of the successive sprays. The lack of similar reductions in the set-back pond is an indication that invertebrate population reductions in the oversprayed pond were probably not due to insect emergence. The fact that chironomid depletion accounted for most of the total invertebrate reduction is not surprising given the relative sensitivity of this taxa and other infaunal species to pyrethroid pesticides (Stephenson 1980, Friesen et al. 1983).

The reductions in mean benthic invertebrate numbers in the oversprayed pond by 50% after the first spray and by up to 90% after all three sprays are similar to the 67% reductions in benthic populations in lotic systems exposed to a concentration of 5 ug/L deltamethrin noted by Dejoux (1979 in Lhoste and L'Hotellier 1982). The ecological significance of such depletions is difficult to assess; however, it can reasonably be assumed that invertebrate reductions of such magnitude would have an impact on energy flow through the pond ecosystem.

5.0 SUMMARY

The rapid disappearance of deltamethrin ($t_{1/2}=1h$) from subsurface water was confirmed, and it was demonstrated that isomerization to inactive (2+2')-deltamethrin is a significant transformation pathway. Evidence from the field and laboratory suggests strongly that volatilization from the surface microlayer is a very rapid process which could be the major route of dissipation of deltamethrin, sprayed on natural waters.

The data collected in this study indicate that when operational sprays of deltamethrin are applied directly to ponds, concentrations of pesticide are sufficient to cause substantial caged and resident invertebrate mortality, as well as some fish lethality. The meteorological conditions which existed at the time of spraying were representative of the range of conditions which can be expected during operational use. Under these conditions the 100 metre set-back was effective in significantly reducing pond deposits associated with aerial drift. The concentrations of deltamethrin in the set-back pond approximated those which are known to be lethal to aquatic invertebrates during laboratory exposures and therefore could have contributed to 40% to 100% mortality of caged invertebrates. There was no immediate fish mortality in the set-back pond.

There was a demonstrated decrease in the ecological integrity of the benthic faunal community in the oversprayed pond as measured by invertebrate abundance on artificial substrates. No changes were observed in the benthic populations of the set-back pond. The utility of the set-back in reducing biological impacts was demonstrated. Set-backs of this type are recommended for the protection of all fisheries-sensitive water bodies. No further reductions in this set-back should be considered without empirical evidence of a lack of biological effects associated with such reductions.

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